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INDUSTRIAL CHEMISTRY

BEING A SERIES OF VOLUMES GIVING A COMPREHENSIVE SURVEY OF

THE CHEMICAL INDUSTRIES

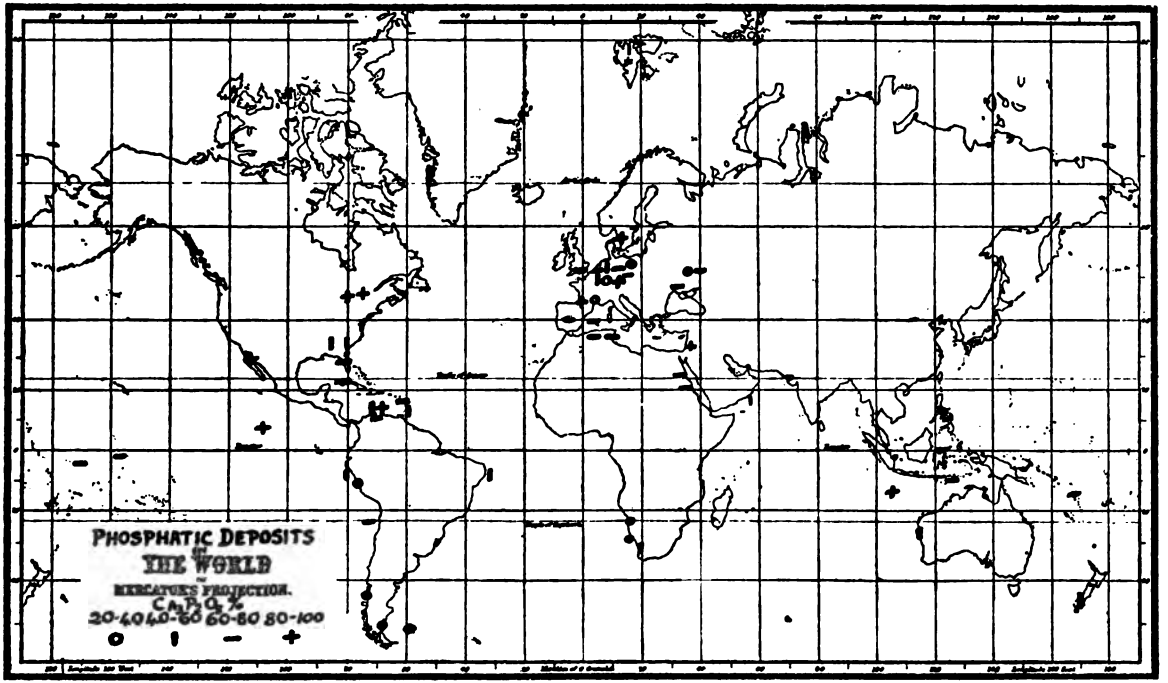
EDITED BY SAMUEL RIDEAL, D.Sc. LOND., F.I.C.

FELLOW OF UNIVERSITY COLLEGE, LONDON

ASSISTED BY

JAMES A. AUDLEY, B.Sc., F.I.C.
W. BACON, B.Sc., F.I.C., F.C.S.
E. DE BARRY BARNETT, B.Sc., A.I.C.
M. BARROWCLIFF, F.I.C.
H. GARNER BENNETT, M.Sc.
F. H. CARR, F.I.C.
S. HOARE COLLINS, M.Sc., F.I.C.
H. C. GREENWOOD, O.B.E., D.Sc., F.I.C.
R. S. MORRELL, M.A., PH.D.
J. R. PARTINGTON, M.A., PH.D.
ARTHUR E. PRATT, B.Sc., ASSOC. R.S.M.
ERIC K. RIDEAL, M.A., PH.D., F.I.C.
W. H. SIMMONS, B.Sc., F.I.C.
R. W. SINDALL, F.C.S.
HUGH S. TAYLOR, D.Sc.
ARMAND DE WAELE, B.Sc.
C. M. WHITTAKER, B.Sc.

&c., &c.



The phosphatic deposits of the world are represented in four different grades according to the percentage of phosphates. No indication is given in the map of the extent of the deposits, only their composition and position being shown. Some of the deposits are in active working order, whilst others are temporarily closed down. New deposits are always being discovered; the general tendency is to increased activity and enterprise in all parts.

Some deposits which contain much iron and alumina are not included, as there is at present no great prospect of their utilization.

CHEMICAL FERTILIZERS AND PARASITICIDES

BY

S. HOARE COLLINS, M.Sc., F.I.C.

LECTURER AND ADVISER IN AGRICULTURAL CHEMISTRY, ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE (UNIVERSITY OF DURHAM) FORMERLY ASSISTANT AGRICULTURAL CHEMIST TO THE GOVERNMENT OF INDIA; AUTHOR OF "HAND-BOOK OF AGRICULTURAL CHEMISTRY FOR INDIAN STUDENTS" AND "PLANT PRODUCTS"

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GENERAL PREFACE

THE rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world. The subject in this series of handbooks will be treated from the chemical rather than the engineering standpoint. The industrial aspect will also be more prominent than that of the laboratory. Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention. Historical notes will be a feature in dealing with the different branches of the subject, but they will be kept within moderate limits. Present tendencies and possible future developments will have attention, and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries. There will be a general bibliography, and also a select bibliography to follow each section. Statistical information will only be introduced in so far as it serves to illustrate the line of argument.

Each book will be divided into sections instead of chapters, and the sections will deal with separate branches of the subject in the manner of a special article or monograph. An attempt will, in fact, be made to get away from the orthodox textbook manner, not only to make the treatment original, but also to appeal to the very large class of readers already possessing good textbooks, of which there are quite sufficient. The books should also be found useful by men of affairs having no special technical knowledge, but who may require from time to time to refer to technical matters in a book of moderate compass, with references to

the large standard works for fuller details on special points if required.

To the advanced student the books should be especially valuable. His mind is often crammed with the hard facts and details of his subject which crowd out the power of realizing the industry as a whole. These books are intended to remedy such a state of affairs. While recapitulating the essential basic facts, they will aim at presenting the reality of the living industry. It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions. A book giving a comprehensive survey of the industry can be of very material assistance to the student as an adjunct to his ordinary text-books, and this is one of the chief objects of the present series. Those actually engaged in the industry who have specialized in rather narrow limits will probably find these books more readable than the larger textbooks when they wish to refresh their memories in regard to branches of the subject with which they are not immediately concerned.

The volume will also serve as a guide to the standard literature of the subject, and prove of value to the consultant, so that, having obtained a comprehensive view of the whole industry, he can go at once to the proper authorities for more elaborate information on special points, and thus save a couple of days spent in hunting through the libraries of scientific societies.

As far as this country is concerned, it is believed that the general scheme of this series of handbooks is unique, and it is confidently hoped that it will supply mental munitions for the coming industrial war. I have been fortunate in securing writers for the different volumes who are specially connected with the several departments of Industrial Chemistry, and trust that the whole series will contribute to the further development of applied chemistry throughout the Empire.

SAMUEL RIDEAL.

PREFACE

In the companion volume in this series, entitled "Plant Products," the chemical fertilizers are only treated from the point of view of crop increment; in the following pages it is rather the sources and modes of manufacture of the chemical fertilizers that take precedence. Nevertheless, no trader can afford to ignore the aims of the purchasers of the commodity he sells or leave out of account the ultimate ends which his manufactures may fulfil. For this reason some slight indication is given of the various purposes to which the chemical fertilizers are applied, and some suggestions are made on the better utilization of the materials at our disposal for improving the produce of land.

The last part of the volume describes some poisons used to combat destructive insects and injurious parasites.

As in the other volumes of the series, references are made at the end of each section for consultation on matter alluded to in the preceding text, whilst a General Bibliography concludes the volume with a list of general works giving information beyond the limits set for the survey in this book.

I have to thank Dr. A. A. Hall, Dr. G. C. Arnott, and Mr. A. Spiller for much assistance in reading the proofs.

S. HOARE COLLINS.

February, 1920.

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CHEMICAL FERTILIZERS

PART I.—THE NEED FOR FERTILIZERS

SECTION I.—PLANT GROWTH WITHOUT FERTILIZERS

HERCULES made no use of the cleanings of the Augean stables; had the ancients placed a high value on animal excreta, such a waste would not have been attributed to a national hero; yet animal manures were used by Egyptians and Chinese from early dates in history. In nature, plant growth proceeds without the use of any chemical fertilizers and without any appreciable amount of materials that could be called manure; but under natural conditions of growth maximum yields per acre are not obtained. Without air, water and soil, no plant growth takes place; a study of such prime needs of plant growth must precede the proper utilization of chemical fertilizers. Many experimental stations have been established all over the world, but few are so well known as the Rothamsted experimental fields, started by Sir John Lawes, and now directed by Dr. E. J. Russell. In the words of Sir Daniel Hall, a former director of Rothamsted, "During the period the Rothamsted wheat-field has been under experiment, the price of wheat has been as high as 75*s*. and as low as 23*s*.; any conclusions reached as to the most paying system at the former price would have to be altogether revised at the lower rates. There is, of course, every probability that price and other economic conditions may fluctuate just as much in the future as they have done in the past, but the one thing that will forever remain unchanged is the manner in which the crop draws its nutrition from the air, the water, and the soil.

Hence the farmer who best knows how this takes place will, other conditions being equal, be the one best fitted to continue to derive a profit under the changing conditions" (see p. 221).

All Plants Need Air.—Air contains one-fifth of its volume of oxygen, which is needed by all parts of the plant, but especially by the roots. Leaves give off oxygen in sunlight in far greater amounts than is required for their life. Air contains four-fifths of its volume of nitrogen, which is not directly used by the plant, but is absorbed by a few bacteria, some of which live in the soil as free creatures, whilst others live in the nodules of leguminous plants. The small amount of argon in the air has no influence on plant life. Air contains carbon dioxide in amounts ranging from 0·03 to 0·04 %; it is absorbed by the leaves, and other green parts of the plant, in sunlight, giving off oxygen and leaving carbon in organic forms for building up plant tissue. Most of the dry matter of the plant is obtained from this source.

Air is needed for the roots, and therefore a soil must contain air and be of open structure, though the need for water precludes a structure which is too open. Cultivation, deep digging and ploughing open up the soil so as to admit air. The soil is also opened by the roots of plants and the movements of creatures like earth worms. The depth to which fresh air will penetrate is greatly increased by alterations in barometric pressure. The passage of water also facilitates the movement of air in the soil. Air is very important in assisting the oxidation in the soil of those substances which are organic or deficient in oxygen. The rate of oxidation is largely modified by alterations in temperature. Below a temperature of 10° C. (50° F.) oxidation is very slow, at about blood heat, 37° C. (98° F.), the best conditions occur, whilst above 50° C. (120° F.) very little bacterial action takes place; at higher temperatures ordinary chemical changes begin to increase in velocity, and hence oxidation will continue. The carbon dioxide in air is not in sufficient quantity to bring about maximum plant production, as, if it is artificially increased, a greater

amount of plant tissue is formed. It is from this carbon dioxide that all the acids, carbo-hydrates, fats, proteins, etc., are produced by the plant. In nature the concentration of carbon dioxide in the air is not constant, but varies over a wide range. The observations at Kew show extreme changes of from 2·43 to 3·60 volumes of carbon dioxide per 10,000 volumes of air, with an average figure of 2·94. As is usually the case in a set of statistics of this sort, the extreme figures are very rare, and do not convey any very accurate mental picture, but if we concentrate our attention on the month of July, when active growth takes place, we find that in 1898 the amount of carbon dioxide was 2·83 volumes of carbon dioxide in 10,000 volumes of air, whereas in the same month of 1901 the corresponding figure was 3·11. It seems highly probable that such a wide range would produce marked influence upon plant growth, and consequently help to distort many of the smaller experimental investigations.

Water Needed by Plants.—A very large portion of any plant is water. In the case of the seeds of most plants the amount of water present lies between 5 % and 15 %, hay and straw between 7 % and 18 %, grass from 50 % to 70 %, green stuff, like cabbages, from 60 % to 80 %, and root crops, such as potatoes, turnips, mangolds and beets, from 78 % to 92 %. Water is used by the plant for the process of transpiration. On the average, one part of dry plant tissue, during the process of its formation, necessitates the evaporation of 300 parts of water through the stomata of the leaves. Under bad conditions of growth this figure can be very largely increased, even perhaps up to 1000, but under good conditions of growth, with a plentiful supply of plant food, such as phosphates, nitrogen, and potash the amount can be markedly reduced.

Water plays a very important part in causing the solution of many of the substances occurring in plant life. Such materials as most of the common salts, like sodium chloride, and some of the simple organic substances, like sugar, belong to the group of crystaloids which dissolve freely in water, giving a perfectly clear solution, passing

through the finest filter, and showing no signs of heterogeneity when observed under a microscope. Some substances of a less constant chemical composition, and of a colloidal nature, only dissolve in water in such a manner that they wholly or partially refuse to pass through the finest filter, and exhibit in the side illumination of an ultra-microscope the appearance of a large number of minute particles in rapid motion. These different kinds of solution behave in a very different manner in passing through the fine walls and minute vessels of a plant.

Hydrolysis is an important function of water and results in very great changes in chemical composition. As examples, one may give the inversion of cane sugar into glucose and fructose, the conversion of proteins into amino acids, and the separation of fats into fatty acids and glycerine. In plant life this hydrolysis is usually effected by enzymes. The reverse of hydrolysis is dehydration, an example of which is the conversion of sugar into cellulose. Enzymes are very active chemical agents produced by vital processes; their action is by no means exclusively limited to hydrolysis, but includes dehydration, oxidation and reduction. It is found by experiment that in a large number of cases the enzyme itself slowly disappears in the course of its activity, although the amount of substance that can be acted upon by an enzyme is very large in proportion to the amount of the enzyme itself. Some preparations of diastase have been prepared of such a strength that they can dissolve 1000 times their own weight of starch. Enzymes, therefore, behave as catalysts, and follow many of the general rules of catalysis. The rate of catalytic change is always in proportion to the concentration of the catalyst, but not always in linear proportion, because some of the catalyst is destroyed. The gradual destruction of the enzyme leads to a retardation of reaction greater than that due to the diminished concentration of the substance undergoing chemical change. Hence the rate of decomposition, when due to an enzyme, generally falls off more rapidly than the logarithmic curve that could be drawn to fit the progress of pure catalysis.

Absorption of Water by the Plant.—The water needed by plants is absorbed by the roots in very nearly every case of plant life. The absorption of water, indeed, constitutes one of the most important of the root functions and is dependent upon the molecular concentration of plant sap in relationship to that of the water in the soil. The laws which govern diffusion follow those of the laws of diffuse matter which are best known in the form of the gas laws. If we imagine 10 grammes of cane sugar existing in the form of a gas, and occupying one litre of space, at a temperature of 14° C., and a pressure of 760 mm., it would be easy to calculate by the ordinary gas laws what pressure it would exert. The molecular weight of cane sugar is 342. That amount of cane sugar would occupy 22·4 litres, at 760 mm. pressure, 0° C., from which we can calculate that 10 grammes of cane sugar occupying 1 litre would exert a pressure of 521 mm. at 14° C. Actual measurements of the osmotic pressure exerted in a porous pot by a solution of cane sugar in water of the above strength, gave figures from 508 to 535 mm., showing that the agreement with theory is very close.

It is the pressure caused in the above manner that forces sap to rise in plants, and to give to plants the great force of suction by which they absorb water from a soil. Since sodium chloride in weak solution ionizes almost completely, it will exert a pressure double that of the amount that sodium chloride would exert if the molecule remained intact. That is to say, a solution of 0·086 % of sodium chloride would exert the same osmotic pressure as 1 % of cane sugar. It is thus easy to perceive why salt will upset the general course of plant life by interfering with, and even possibly reversing, the osmotic pressure normally developed. When water is drawn out of a living plant by soluble salts, plasmolysis sets in, and the protoplasm shrinks. Excessive amounts of very soluble fertilizers can do harm by setting up such an interference with normal conditions of growth.

The Soil Conditions Suited to the Growth of Plants.—Plants need a soil which is sufficiently open to admit of root penetration and a ready movement of air and water. If the

texture of the soil be too close, all these processes fail. On the other hand, if the texture be too open, water will flow away too easily, and the growing plants be liable to suffer from drought. The porosity of a soil is dependent upon a large number of factors. The size of the soil particles, the condition of aggregation in which these particles lie, and the form of packing of the soil particles and soil aggregates are all matters which markedly affect the porosity of the soil. The addition of lime to the soil collects the particles into large aggregates, which behave as if they were loosely packed and possessed a more open structure, thereby assisting the flow of air and water. These results will be produced by fertilizers containing lime like basic slag or by compound fertilizers containing carbonate of lime. Compounds containing soda, such as nitrate of soda, for example, break down these aggregates, and ultimately produce a closer packing of the soil particles, thus checking the movement of roots, air and water. Wood ashes, which contain potassium carbonate, act in a similar manner. Turning the soil over gives a loose packing, trampling and rolling give a tight packing. Deep cultivation gives a great depth of soil, which, with certain limitations, is almost equivalent to an increased area of surface.

The Soil Needs Plant Food.—Nitrogen, phosphorus and potassium take the first place in the list of plant foods. There are other elements, such as calcium, sulphur, chlorine and sodium, which may be needed in special cases. Calcium, in the form of calcium carbonate, plays an important part in regulating the physical character of the soil, and it is not necessary to account for it twice, both under its physical and chemical aspects. Sulphur is supplied by the smoke in the vicinity of towns, but in districts remote from industrial factories it may be necessary to apply sulphur to certain crops. When this is the case, an application of super-phosphate or sulphate of ammonia will generally be found the most suitable method of supplying sulphur, since the sulphur is obtained in these articles without any cost, the price of such articles being dependent upon their phosphorus or nitrogen contents (see p. 188). Sodium and chlorine are needed for

certain particular plants, especially those bred from wild forms growing in districts near the sea. For many plants the amount of salt spray blown in from the sea will be sufficient, but in inland districts the amount of salt may need to be increased before intensive plant production can take place. It is only certain crops which require these substances as fertilizers. Sodium has a wider range of usefulness than chlorine (see p. 69).

Availability of Plant Food in the Soil.—Cultivation and the activities of earth worms and bacteria render plant food in the soil more easily available to the plant. Organic manures and vegetable refuse form valuable materials for supplying the necessary food for earth worms and bacteria to live upon. Deep cultivation also assists in making the plant food in the soil more easily available, because it admits air which stimulates living things in the soil. Many methods have been adopted for attempting to measure the amount of available plant food in the soil. The amounts washed out by water are so small as to be difficult to measure, and therefore weak acids have commonly been employed. The method in use in this country is most generally Dr. Dyer's citric acid method, in which the soil is shaken with a 1 % solution of citric acid. The results of this method have been carefully correlated at Rothamsted, and experience in many parts of the world have shown the value of this method. The results of other solutions which have been sometimes employed in other countries have shown results possibly as good, but certainly no better than Dyer's method.

Soil Water.—Variations in the carbon dioxide content in the air of the soil will also cause variations in the concentration of carbon dioxide in the water of the soil. As a result, the concentration of hydrogen and carbonic acid ions will be much increased in the soil if rapid oxidation of soil organic matter is taking place. Like all the other acids that have been used in the efforts to extract the available plant food from the soil, carbonic acid gives soil solutions which increase in strength more or less in proportion to the carbonic acid supplied, and hence the concentration of soil solutions will

be much modified by vigorous oxidation of organic matter in the soil; some of the beneficial actions of organic matter in the soil must be attributed to this action. Since bacterial action in the soil may easily be very markedly influenced by increasing the supply of phosphoric acid and nitrogen, the amount of carbonic acid in the soil will also be indirectly modified by the application of chemical fertilizers; hence it comes about that the addition of one element of plant food in the form of a plant fertilizer may easily render available some other element, provided the soil was already fairly rich in that material.

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Section II.—THE INCREASE OF CROPS BY THE USE OF FERTILIZERS

Crop Stimulation and Nitrogen.—Any substance added to the soil which produces an increase in the crop may be called a fertilizer, but an increase in the crop produced by any physical or mechanical means which improve soil condition is not considered a fertilizer. A garden spade unquestionably increases crop production, but it is not called a fertilizer. In the same way, the addition of sand to clay or clay to sand will increase crop production, but neither clay nor sand are considered to be fertilizers. It is necessary to restrict the term fertilizer to substances having a specific action on plants, followed by an increase in growth.

Nitrogen, phosphorus and potassium are the chief elements having a specific fertilizing effect. The most important compounds of nitrogen that occur in fertilizers are nitric acid, ammonia, amides and albuminoids. Of these the nitrates are very fully oxidized compounds, and are produced in the soil from ammonia by bacterial action and oxidation. Similarly, ammonia is obtained from amides, amino acids and other simple organic compounds containing nitrogen. These, in their turn, are obtained from albuminoids which have been decomposed by bacteria and larger forms of life.

The Result of the Application of Nitrogen.—Applications of soluble nitrogenous manure are speedily indicated by the deepening green colour of the crop, by greater development of leaf and increased growth of stem. Judged from its most obvious visible results, the main function of nitrogen seems to be an increased production of leaf and stem. The deficiency of available nitrogen in a soil is at once shown in the stunted growth of stem and the yellow tint of leaf.

Excessive applications to the cereal crops of nitrogenous manures frequently cause those crops to "lodge," or fall down in wet weather, owing to the effect on the leaf and stem of excessive growth, stimulated by too much nitrogen; at the same time, the quality of the grain is often inferior, and the date of ripening unduly delayed. The general tendency of heavy dressings of nitrogenous manures is to increase the period during which ripening takes place, and, in the case of root crops, to lower their keeping qualities, to render them more watery, and to increase their susceptibility to fungoid and bacterial decay. Nevertheless, sufficient quantities of available nitrogen are absolutely essential for large crop yields. On the lighter soils in the wetter climates, sulphate of ammonia is generally preferable to nitrate of soda, but much will depend upon the amount of available lime and upon the other fertilizers which the farmer proposes to use. The general result of the addition of nitrogen as applied to the crops at Rothamsted can be best described by quoting from Russell's "Soil Conditions." He says: "The first addition of nitrate causes a marked rise in the weight per grain and the proportion of grain to total produce, but successive additions show no further rise. Indeed other experiments prove that excess of nitrogenous food causes the proportion of grain to fall off somewhat. The leaf and the general character of growth are affected to a much greater extent. Nitrogen starvation causes yellowing of the leaf, especially in cold spring weather, absence of growth, and a poor starved appearance generally: abundance of nitrogen, on the other hand, leads to a bright green colour, to a copious growth of soft, sappy tissue, liable to insect and fungoid pests (apparently because of the thinning of the walls and some change in composition of the sap) and to retarded ripening: the effects resemble those produced by abundant water supply. A series of plants receiving varying amounts of nitrate are thus at somewhat different stages of their development at any given time, even though they were all sown on the same day, those supplied with large quantities of nitrate being less advanced than the rest. If they could all be kept under

constant conditions till they had ripened this difference might finally disappear, but in crop production it is not possible much to delay the harvest owing to the fear of damage by autumn frosts, so that the retardation is of great practical importance. Seed crops like barley that are cut dead ripe are not supplied with much nitrate, but oats, which are cut before being quite ripe, can receive larger quantities. All cereal crops, however, produce too much straw if the nitrate supply is excessive, and the straw does not commonly stand up well, but is beaten down or "lodged" by wind and rain. Swede and potato crops also produce more leaf, but not proportionately more root or tuber, as the nitrogen supply increases; no doubt the increased root would follow, but the whole process is sooner or later stopped by the advancing season—the increased root does in fact follow in the case of the late-growing mangold. Tomatoes, again, produce too much leaf and too little fruit if they receive excess of nitrate. On the other hand, crops grown solely for the sake of their leaves are wholly improved by increased nitrate supply: growers of cabbages have learned that they can not only improve the size of their crops by judicious applications of nitrates, but they can also impart the tenderness and bright green colour desired by purchasers. Unfortunately the softness of the tissues prevents the cabbages standing the rough handling of the market." Some of the results obtained at Rothamsted in studying the stimulative effect of nitrogen, are exhibited in a very brief form in Table 1.

TABLE 1.

ROTHAMSTED, BROADBALK FIELD, WHEAT.

Average of 61 years.

Manure.	Dressed grain (bushels).	Straw (cwt.).
Unmanured	12·6	10·3
Rape cake	25·4	25·7
Farmyard manure	35·2	34·8
200 lbs. ammonia salts and mixed minerals ..	23·2	21·4
600 lbs. ammonia salts and mixed minerals ..	36·6	41·1

In Table 1 it may be seen that, contrary to anything one might have reasonably expected, farmyard manure has not exhibited that striking superiority over artificial manures that general farm experience would have suggested. At Rothamsted the rainfall is not, perhaps, quite the lowest in the British Isles, but it is a long way below the average, and one would expect that so much farmyard manure, applied for so many years, would have enabled the soil to regulate the water supply in such a manner as to give the organic manure an advantage over chemical fertilizers. As a matter of fact, chemical fertilizers have beaten farmyard manure over a stretch of so many years as to rule out altogether any temporary or accidental influence. This important fact, that nitrogen can be applied for so many years without any exhaustion of the soil, has enabled Great Britain, during the war, to increase her wheat yields by applications of sulphate of ammonia. Had her government not been aware of Rothamsted and its results, which had been copied and confirmed under numerous and varied local conditions, it would have been impracticable to have proceeded with the vigorous wheat production that has taken place during the war. Many wonderful things have been done during the war, but probably there is nothing that can beat the achievement of a country that had previously failed to produce one-fifth of its breadstuffs, increasing its yields in so short a time under the stress of war, that it was able to bring the production of breadstuffs up to more than three-quarters of its requirements (see p. 180).

Root Growth with Phosphorus.—Of the oxides of phosphorus it is only phosphorus pentoxide that is concerned with any of the fertilizers. Phosphorus pentoxide by hydration gives meta-, pyro- or ortho-phosphoric acid according to the amount of water that is taken up. In a soil, the phosphoric acid exists in combination with calcium, iron or organic matter. In some fertilizers pyro-phosphoric acid may occur, as, for example, in super-phosphates that have been overheated during the process of drying.

Applications of phosphatic manures do not produce

such obvious results on the general appearance of the crop to which the manure has been supplied as do similar applications of nitrogenous manures. The development of grain and root, however, appears to be very intimately connected with the supply of phosphorus. The proportion of grain to straw is generally increased, and the period of ripening shortened. The increased development of seedlings when well supplied with phosphates is very marked. A very striking instance of this result is the increased growth of the young turnip plant after it has received an application of phosphatic manure. As with nitrogen, a sufficient amount of phosphorus is necessary for the complete development of all crops. A very striking result of the application of fertilizers containing phosphorus, is the extent to which root formation is encouraged. As long ago as 1847 Lawes wrote :—"Whether or not superphosphate of lime owes much of its effect to its chemical actions in the soil, it is certainly true that it causes a much enhanced development of the underground collective apparatus of the plant, especially of lateral and fibrous root, distributing a complete network to a considerable distance round the plant, and throwing innumerable mouths to the surface."

The effect of another phosphatic manure, basic slag, on old land hay, is as striking as the results on grain alluded to by Lawes. At Cockle Park, in Northumberland, the Palace Leas hay field very strikingly demonstrates the effect of continued application of phosphatic manures on the fibrous development of the roots of the grasses and other plants growing in ordinary herbage. Where phosphates are absent the tendency is to develop a thick mat of useless grass, which appears to act as a thatch, keeping rain from penetrating into the soil underneath, so that root development is very feeble. On the other hand, where phosphates are used in large quantities, the roots break up the soil, and convert a very indifferent clay into a fair loam. These results follow from the changed bacterial and fungoid decompositions of organic matter in the soil which are induced by the kind of fertilizers applied to the hay field. Where much acid manure

is used the turf smells foul, but with basic slag and potassium chloride a sweet-smelling turf is formed.

Equally striking results are shown on land which is grazed. On the unmanured plot, yellow clay still remains close to the surface, yet on the plot that has been manured for over twenty years with basic slag a very useful loam soil extends 10 ins. or 12 ins. from the surface. The steady downward trend of the roots and the fibrous loam appears to be still continuing. Dressings of phosphates are particularly valuable where greater root development is required. They are not quite so much needed on sands, because great root formation takes place on these soils in any case. In a particular corner at Palace Leas, where the soil happened to be somewhat sandy, the marked differences alluded to above are not so easy to observe. In addition to what has been said above, phosphates are used with great effect on all root crops, such as swedes, turnips, potatoes and mangolds, and they are also found necessary for the growth of barley. They have been found especially valuable where droughty conditions are experienced. In India it has been discovered that phosphates can be made to save irrigation water, and in New Zealand the application of phosphates, even of the most insoluble kinds, has produced marked and valuable results. Phosphates, moreover, promote early ripeness and shorten the period of growth; they are extremely valuable for accelerating the ripening of crops in districts and climates where there is ordinarily much risk of loss by persistent bad weather. The most northern limit to which wheat production in Canada can be pushed is partly dependent upon the supply of phosphates, and, given ample supplies, there is little doubt that the limit of wheat cultivation could be pushed still further north. It has always been noticed at Rothamsted that the barley plots that have been manured with phosphates are ripe while the others are still green. In spite of what has been said above of the extraordinary value of the phosphates, the results are not as striking as those shown by nitrogen compounds. There is not such an obvious change in the appearance of the plant grown with a full supply of phosphates as there is

when the crop is well fertilized with nitrogen compounds; it requires to have a controlled plot side by side to be able to draw attention to the result. It is generally on the heavy clay soils, deficient in both lime and phosphates, that basic slag has produced most obvious and marked results. It is one of the most striking scenes, on a clear day, at certain seasons of the year, to ascend the tower at Cockle Park, look over the experimental plots on the farm, and observe the extraordinary variety of colour that meets the eye, due to the different treatment the plots have received. Those receiving liberal dressings of phosphates are brilliantly green, while those that have been badly treated are a dull, unhealthy yellow. It is an old farming tradition that pastures are improved by grazing with stock that receive generous rations of rich food in addition to what they pick up for themselves; chemical fertilizers can produce the improvement in less time and at less cost. The relative importance of phosphatic manures to nitrogenous and potassic manures on certain types of soil is best described by quoting Gilchrist's comments in the Cockle Park "Guide to Experiments for 1918": "On the great bulk of poor pastures on the heavy soils of Northumberland, basic slag is the most effective manure for economic improvement, and on the lighter soils the same manure, along with a potash manure, has also been found to be most effective. The question has also been settled that second and even up to sixth dressings of slag are quite as effective as first dressings. The after-effects of feeding cake to grazing stock are far from proving as satisfactory as was expected."

"For old land hay active nitrogenous manures have been shown to deteriorate greatly the feeding value of the hay, while phosphatic manures, combined with potash manures if necessary, have greatly developed clover and improved the feeding value of the hay. In combination with dung, slag has been found to be the best artificial dressing for old land hay, probably because the dung contains sufficient nitrogen and potash, while slag supplies phosphates and lime in sufficient quantities and in a suitable condition to act with dung.

"The improvement in the hay and pasture at Cockle Park, especially in the quality of both, has enabled a much larger stock to be kept with considerably less expenditure on concentrated feeding stuffs. The better feeding quality of the hay has reduced the amount of cake and meal needed in the winter, and the better feeding quality of the pasture, especially of the winter foggage, has enabled the grazing stock to depend to a much greater extent on the pasture."

At Cockle Park basic slag, superphosphate and dissolved bone have all been experimented with, and, provided other conditions are satisfactory, phosphatic manures, whatever their nature, give somewhat similar results. The phosphatic manures used have shown an increase per acre of £1, as measured by the mutton produced by sheep grazing. As, however, basic slag is very much cheaper than either of the other two, counted in terms of the amount of phosphorus supplied, it can be confidently recommended even in bleak districts. The more expensive forms of the phosphorus manures may yield results which are satisfactory enough, but unless large increases in crop are obtained there is a difficulty in making a sufficient profit to cover the cost of the fertilizers. With sufficient rainfall, protection from wind and good working soil such increases are frequently made, but in bleak and backward districts sufficient increase cannot always be obtained. Where general farming conditions and prospects are poor, basic slag is usually preferred, but with good soils and markets, superphosphate is more commonly used.

One great result of the development of root action by the use of phosphatic manures is to make the soil easily penetrated, not merely by roots, but also by air and water. The soil then becomes the home of a large population of various forms of soil life, varying in magnitude from bacteria to earth worms. Experiments which have been made on the results of applying certain particular forms of phosphoric acid to the soil show that the pure forms of ferric phosphate, aluminium phosphate and calcium phosphate give increases of crop. Superphosphates, however, produced far better

results than any of the pure chemical substances. The superiority of superphosphate is very often due to the fact that, being soluble, it distributes itself in the soil much better than less soluble compounds. Where there is permanent herbage, rapidity of action is of less account, and distribution is somewhat slow, since manure applied to a pasture must penetrate the matted surface before it can reach the true soil. Any phosphatic manure applied to a soil is, in any case, rapidly fixed in a relatively insoluble form, but the more finely divided the fertilizer is, the better will be the distribution. The effect of phosphates, in raising the quality and feeding value in hay crops, is a very important point. The most nutritious pastures in England and the best dairy pastures in France are those that are richest in phosphates, and it has also been shown that the best wines contain the greatest quantity of phosphoric acid, and that there is a close connection between the amount of phosphates in the soil, the amount of phosphates in the wines, and the quality of the wines.

As has been indicated above, many of the ultimate effects of phosphatic manures must be attributed to secondary results. Basic slag applied to the soil on Tree Field at Cockle Park not merely gave an increased quantity of mutton and hay, but also almost doubled the proportion of phosphoric acid in the hay, so that the amount of phosphoric acid consumed per acre by the animals was quadrupled by the addition of phosphatic manures. The percentage of nitrogen in the soil is also increased very markedly. As the result of eleven years' treatment on Tree Field, the amount of nitrogen in the soil has been increased from 0·185 to 0·236, where slag and superphosphate have been used. That is to say, the nitrogen has been increased to the extent of about 850 pounds of nitrogen per acre. When nitrogenous manures, sulphate of ammonia in some years and nitrate of soda in others, were used on other plots, very little increase in nitrogen took place. Some of the results obtained by using basic slag are really due to the fact that the soil has become very much richer in nitrogen, but, of course, the whole credit of

this must be put down to the basic slag, as it alone is responsible. As phosphatic manures are hardly lost by drainage to any appreciable extent, the phosphates are only removed from the soil in the form of crops or stock. Smetham some years ago gave an interesting account of the income and expenditure of phosphates in the British Isles, and showed that the country was not really gaining in phosphates, in spite of the large applications that had been made, and it follows that it is urgently necessary that phosphatic manure should be pushed ahead very rapidly, so as to make allowance for increased population and increased crop production. When phosphatic manures are used at the rate of 1 cwt. high-grade basic slag per acre per annum the soil is steadily gaining in phosphates.

TABLE 2.

COMPARATIVE RESULTS OF DIFFERENT ELEMENTS OF PLANT FOOD ON THE GROWTH OF BARLEY AT ROTHAMSTED.

	Yield of grain (pounds per acre).		
	20 years. 1852–71.	20 years. 1872–91.	20 years. 1892–1911.
Farmyard manure	2772	2770	2530
Complete chemical fertilizers	2630	2290	2135
No phosphates	1990	1530	1245
No potash	2660	2150	1720
No nitrogen	1552	950	840

TABLE 3.

COMPARATIVE RESULTS OF DIFFERENT ELEMENTS OF PLANT FOOD ON THE GROWTH OF BARLEY AT ROTHAMSTED.

	Yield of straw (pounds per acre).		
	20 years. 1852–71.	20 years. 1872 91.	20 years. 1892–1911
Farmyard manure	3168	3325	3445
Complete chemical fertilizers	3185	2620	2595
No phosphates	2322	1695	1655
No potash	3092	2250	2030
No nitrogen	1612	945	1145

Some of the results of phosphatic manuring at Rothamsted are summarized in Tables 2 and 3, which show the amount of grain and straw yielded in three successive periods of 20 years each, under different treatments.

During the many years in which barley was continuously grown, none of the methods employed quite maintained the yield, but the farmyard manure nearly achieved that object. Complete chemical fertilizers have clearly failed somewhat in this respect, but nothing like as strikingly as unbalanced fertilizers lacking some important ingredient. It will further be noticed that the most serious omission is nitrogen, and the least important omission is potash, but this relationship largely depends upon the characteristics of the soils; it is only on light soils that potash is essential. With reference to the straw, the use of farmyard manure has enabled the soil to do more than maintain its position. Again, it will be seen that nitrogen is more essential than phosphates, and phosphates more essential than potash. Barley does not seem to permit of the replacement of farmyard manure by artificials quite so readily as wheat does.

The question as to whether phosphates have a specific effect on transpiration in crops has been specially inquired into by Leather in India. Many of the soils that he experimented upon were markedly deficient in phosphates, and responded to phosphatic manures, hence arose the question whether the increased economy of water was due to the specific effect of phosphates, or merely due to supplying a soil with the particular element of plant food most needed. He therefore employed a soil which apparently did not require phosphatic fertilizers, as judged from the crops produced, and in this case he found that the best plants and the lowest transpiration ratios were obtained from the use of purely nitrogenous fertilizers. He thus demonstrated that the effect of superphosphate in the previous experiments has been entirely due to the deficiency in this soil of readily available phosphates, and not to any specific action on transpiration by phosphates themselves.

Leaf Development with Potassium.—All the potassium

salts suitable for manure are soluble in water. Any ordinary soil contains an ample supply of insoluble potash compounds, and, whatever salt may be added to the soil, the potassium contained in it is readily fixed near the surface. Potash is very intimately connected with the process of carbon assimilation by the green parts of a plant. Applications of potash manures to plants stimulate the synthesis of carbo-hydrates, such as sugar and starch. Potash tends to improve the quality of grain and roots; it is also particularly powerful in promoting the development of leguminous crops, although these latter have a very strong power of extracting potash from very insoluble potash compounds, provided they are supplied with a sufficiency of phosphatic manure.

When the supply of potash to the plant is quite insufficient, the leaf loses its natural green tint, and presents an abnormal appearance. Potash-starved plants exhibit a very poor colour, and their leaves have a tendency to wither at the tips and edges. The production of sugar by swedes and the production of starch by potatoes is very intimately connected with the supply of potassium compounds. In experiments at Rothamsted 7255 pounds of leaves accompany 14,684 pounds of mangolds where potash food was deficient, but where potash was supplied the production of leaf amounted to 8508 pounds, and of root to 40,328 pounds. Thus with less than 20 % increase of leaf there was nearly three times as much root. Unlike phosphates and nitrates, potassium compounds have a very marked effect on the weight of the individual grains of barley; poor, stunted grains may very easily be produced by withholding potash. Potash-starved plants are the first to succumb in a bad season, whilst those plants that are over-manured with nitrogen exhibit the same lack of resisting power under unfavourable weather conditions. The leguminosæ also seem to stand in considerable need of potassium salts. Potash is well known as a good stimulant for clover, especially on light soils where potash is naturally deficient. The effect on barley of potash salts is given in Tables 2 and 3 (p. 18), which show that potash is less important than

nitrogen or phosphorus on that crop and soil. Generally speaking, Great Britain is not a country where marked deficiencies of potash occur; it is only on particular soils that this element is needed. Potash appears to be partially replaceable by other substances, such as soda, magnesia, and lime; it is possible that this replacement is sometimes due to double decomposition in the soil. Over an average of 61 years at Rothamsted, the loss due to replacing potash by soda is rather less than two bushels of grain per annum, and the loss from replacing potash by magnesia is very slightly greater. Similarly, about 3 cwts. of straw per annum are lost by the same procedure. In comparison, the loss due to leaving out farmyard manure is 23 bushels of grain. It is, therefore, practicable on soils moderately supplied with potash to go on farming for many years with few applications of potash. Where a farm is formed of very heavy clay land, the judicious application of phosphates to land under hay will indirectly remove a very large quantity of the potash from the clay of the soil. Some of this potash will return to the manure heap, and thence to the arable land, provided that the manure heap is well cared for. Where, however, a farmer has little heavy land, there is small chance of his escaping the purchase of potash fertilizers if he wishes to maintain the fertility of his fields.

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PART II.—THE SOURCES OF FERTILIZERS

SECTION I.—MINERAL DEPOSITS OF FERTILIZERS

Nitrate of Soda.—Chemistry is a fundamental science, and therefore any substance may be considered as a "chemical." The terms "chemical fertilizers," and "artificials," are intended to imply all materials which produce some specific increase of crop, excepting farmyard manure or similar substances made on the farm. Nitrate of soda is not a substance that could be manufactured on a farm, and is a plain, simple salt, providing no ambiguity as to its classification.

The nitrate of soda industry has developed in Chili from the small beginnings made in about 1830 to the large developments of to-day. The business has been so interfered with by the war that it is a little difficult at the present time to forecast its future. Large quantities of nitrate of soda have been used in agriculture, but there are also considerable quantities used for the production of gunpowder and other explosives. Nitrate of soda is produced nowhere else in the world outside of the northern provinces of Chili; the only other natural product of a similar kind is nitrate of potash, which is obtained from certain soils in India and Burma, and, to a lesser extent, in Africa. Hitherto the proportion of nitrate of soda used in the British Isles has been comparatively small, but it must not be forgotten that sulphate of ammonia is a home product, which can be used in place of nitrate of soda in many instances. A question of considerable interest arises:—Why should northern Chili be so different from any other part of the world as to be the

sole natural repository of nitrate of soda? If we first consider the topographical and climatic conditions of the northern provinces of Chili, we find them to be quite abnormal. Excepting for small fractions of the southern part of the nitrate deposits, the district which yields nitrate of soda lies in the tropic of Capricorn. Rain only occurs at infrequent intervals, there being often no rain for a whole year; when rain falls it merely wets the surface of the ground, although there are rare occasions when local floods may prevail. Had there been much rain, the nitrates would have been washed away long ago. The dryness of this particular coastal region is due to the cold south polar wind, which is colder than the local atmosphere and blows from the coast towards the nitrate region according to the rough sketch in Fig. 1. It is noticeable that the places where

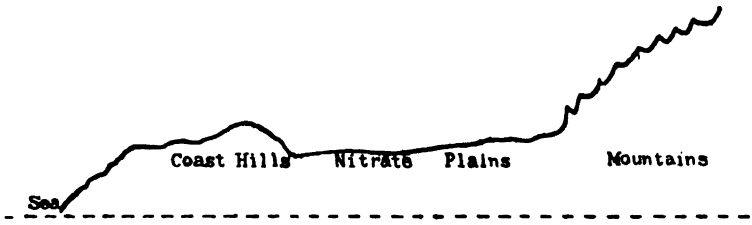

FIG. 1.—Section of Chili nitrate region.

The wind blowing over the sea does not bring moisture on to the land because it is a cold wind from the antarctic regions. Passing inland the wind becomes heated and drier, but after crossing the dry plains it rises up the steep slopes of the Andes, where it expands, cools, and deposits moisture. The drainage from the mountains percolates through the soil and dries up, forming the deposit of caliche.

the nitrates are deposited are cut off from the sea by a low range of coastal hills; also that they lie at the lowest point of an extensive plain, bounded on the inland side by the high mountains of the Andes. With such a section before one, there can be little doubt that the nitrates result from slow drainage from mountain ranges, which has accumulated in the low levels from which there is no exit to the sea. The nitrates have doubtless originated by a slow process of oxidation of organic matter in higher regions of the mountains. As the soil contains a fair amount of sodium,

and but very little potassium, the chief product is nitrate of soda. The nitrate strata are covered with a few inches of loose-blown dust, under which is a hard rock containing much nitrate, some common salt, magnesia, earth and pebbles. The true caliche is found some 20 or 30 ft. below the surface, under which there is a loose layer of gravel, containing no nitrate. Bands of sulphate of lime and clay also occur. Caliche, which varies in thickness and quality, is a mixture of nitrate of soda, a little nitrate of potash, a large amount of common salt, and, very frequently, sulphate of soda and magnesia. A good deposit would consist of a bed, about 3 or 4 ft. in thickness, containing from 40 % to 45 % of nitrate. There are, besides, many beds which do not contain more than between 5 % and 20 %, but up to the present these have been little worked.

The general method of procedure is for a man to clear away the wind-blown dust on the surface, and then cut a round hole, about 9 ins. in diameter, through to the bottom of the caliche. The hole is then enlarged, and a small boy is sent down to clear it out still more, especially at the base. A cup is thus formed underneath, which is filled with gunpowder, and subsequently blown up. After the explosion workmen break up the blocks with crowbars, and fill the material into carts. The composition of the caliche varies considerably, the kinds most commonly worked containing from 20 % to 50 % sodium nitrate, 25 % to 60 % sodium chloride, from 2 % to 20 % insoluble matter, about 5 % sodium and magnesium sulphates, with occasional amounts of iodides, iodates and perchlorates.

Nitrate of Potash.—Nitrate of potash has been one of the important smaller industries of India from very early times ; it depends for its raw material upon earth which is collected from old, as well as from existing, village sites. Indian villages consist of small buildings, chiefly composed of mud, the floors of which are often made by beating down mixtures of mud and cow dung. After many years these mud huts tumble down, and bury considerable quantities of miscellaneous organic refuse. Sometimes the villages

are just rebuilt on top of the old débris, whilst in other places the buildings are erected a little apart from the old site. There is, therefore, a tendency for these villages to be somewhat raised above the general level of the plain, owing to the accumulations of mud and refuse for, possibly, thousands of years. The decaying organic refuse in these sites undergoes the process of nitrification, and drains into some of the lower levels. The earths from which the crude saltpetre is obtained contain very varying amounts of nitrate, as little as 1 % and as much as 29 % having been observed, but few beds of nitre earth contain more than 5 %. In addition to nitrate, the earth always contains sodium chloride and sodium sulphate in considerable amounts.

The general method of extraction consists in building a small earthen chamber, with a hole in front to allow the nitrate liquors to drain away. A false bottom of bamboos and matting is placed in this earthen chamber. The earth is laid on this false bottom, and trodden into position with much care. Small quantities of wood ashes are very frequently mixed with the earth during the process of filling. Water is now poured on to the surface, in such a way as to avoid disturbing the earth. As the water soaks into the earth, the clay begins to swell, and the rate of drainage becomes very slow. The water soaks down slowly, and after the lapse of a few hours, reaches the bamboo floor and drains away out of the hole in the front. As the water slowly trickles downwards, the most soluble salts are in excess and produce a saturated solution, whilst the less soluble salts are to a large extent left behind. At the same time, double decomposition takes place between any calcium nitrate in the earth and any potassium carbonate in the ashes with which the earth has been mixed. As these earths always contain much organic matter, the drainage is usually coloured brown. The composition of the drainage liquors varies considerably, but is given approximately in Table 4.

TABLE 4.

NITRE-EARTH DRAINAGE LIQUORS.

	Per cent.
Potassium nitrate	7·24
Potassium chloride	0·4
Sodium chloride	15·25
Calcium chloride	0·1
Magnesium chloride	0·2
Calcium sulphate	0·1
Magnesium sulphate	0·1

This liquor is either boiled down in iron or earthen pans by means of heat from burning wood, or is allowed to concentrate in shallow trays by sun heat. The latter method is chiefly used in the Punjab. As concentration proceeds, sodium chloride is first deposited, especially when the operation is conducted over a fire at a temperature approaching boiling point. In this last case, when the liquors have been sufficiently concentrated, they are allowed to cool, and the saltpetre crystallizes out. The saltpetre so obtained is usually sent to a refinery for the manufacture of gunpowder, but the crude materials are sometimes used for manure. The nitre earths are also used directly for manurial purposes. The finished crude saltpetre varies considerably in composition from 25 % to 75 % : sodium chloride is an invariable impurity, and sodium sulphate is usually present to some considerable extent. Typical analyses are given in Table 5.

TABLE 5.

CRUDE NITRE.

	High grade (per cent.).	Low grade (per cent.).
Potassium nitrate	66·07	26·86
Magnesium nitrate	2·54	12·24
Sodium chloride	21·84	34·80
Sodium sulphate	3·65	11·20
Insoluble matter	0·90	1·40
Water	5·00	13·50

It is probable that the existing sources of potassium nitrate in India might be further utilized ; artificial nitre beds might be established there. Deposits of nitre, derived from rabbit dung, occur in the Griquatown and Pretoria beds, South Africa.

Rock Phosphates.—Most of the mineral phosphates are probably derived from various animal sources. Sea birds, nesting on grounds above rocks in which limestone or calcareous materials of some kind constitute the major part, will supply the phosphates. When rain falls upon such nesting grounds, the drainage waters contain considerable quantities of soluble phosphates, such as K_2HPO_4, which, coming into contact with the calcium carbonate of the limestone, convert the latter into calcium phosphate, potassium bi-carbonate being leached out. The drainage follows the lines of the fissures in the limestone, and subsequently pockets of calcium phosphate will be formed in the limestone or chalk. In some cases the deposits of phosphates may be concretions which have formed in chalk or calcareous soils. In other cases, rock phosphates are partly water-washed guano, in which the soluble parts have been removed, and the less soluble fractions, consisting largely of calcium phosphate, left behind. These materials are frequently washed by rivers or running water, and perhaps transported considerable distances as gravel. They may have even undergone a certain amount of separation from other alluvial ingredients, according to their degree of density or hardness. The theory that all phosphates are of organic origin is demonstrated by the test that when ground very finely, or dissolved in acids, they all give the same "paraffin oil" smell. They are, therefore, not likely to be very ancient or very much metamorphosed. In the frontispiece is a map which shows the chief phosphatic deposits worked within recent years. In populous districts, where the demand for phosphates is great, diligent search for deposits has often been successful. In unpopulous regions, it must not be assumed that there are no deposits because they are not marked on the map, but rather that search may not have been sufficiently diligent, and that the future may reveal deposits, as yet unsuspected.

As a general rule, phosphates are dug in a similar way to gravel, but sometimes they are washed out by jets of water under high pressure. They are usually dressed over screens, and sometimes even lixiviated. By these means the

phosphates may be graded up so as to produce an article with a percentage sufficiently high to justify carriage.

English Sources.—The English sources are mostly worked out. Various coprolites in Cambridge, Suffolk, and Somerset contain from 50 % to 60 % of phosphate and from 2 % to 30 % of calcium carbonate. These deposits are very largely concretions, and are now little utilized, owing to the competition of foreign phosphates. Some of these phosphates are fossil bones of animals living in prehistoric times.

Canadian Sources.—Deposits of apatite in Ontario and Quebec have been worked for a long time, but have now been given up, as the costs of production were almost prohibitive, owing to the high costs of labour and transport. These apatites contain fluorine equal to 6 % or 7 % calcium fluoride.

Oceania.—Many of the islands in Oceania and the Pacific possess deposits of guano, some of which have been washed out by rain to such an extent that there is little organic matter or nitrogen left, while the phosphates have been concentrated up to 80 %. In addition to these, there are in New Zealand deposits of phosphatized limestone, containing 50 % phosphate of lime, which can be excavated like gravel. Christmas Island, south of Java, yields a phosphate of about 80 % strength, which is very suitable for superphosphate manufacture.

United States of America.—Many deposits of phosphates in the United States have been discovered and worked with characteristic energy. Some of the best known of these are the Florida phosphates, which consist either of hard rock phosphates, containing 80 % calcium phosphate, or soft clay phosphates, containing about 40 % to 60 % calcium phosphate. Phosphates from the Peace and Alabama rivers are obtained largely by dredging. Tennessee contributes some phosphates which are mostly discovered in veins or pockets; they are easily obtained without much labour or washing as a grade of 60 % to 70 % phosphates. Of somewhat less importance are the deposits in Carolina, which extend from North Carolina into South Carolina, forming

a coastal belt containing both land and river phosphates. The land phosphate is usually excavated, whilst the river phosphates are often obtained by dredging. These phosphates are not so rich as those of some of the other deposits, but can be concentrated up to 50 % or 60 % strength.

African Phosphates.—At Tunis and Algeria very large deposits of phosphates occur, those produced near Gafsa being somewhat soft, gravelly phosphates, containing 55 % to 65 % calcium phosphate. In different parts of these two countries, there are other rock phosphates which are harder and more stony. Some of the larger lumps of these mineral phosphates show a high content of calcium phosphate on the outside, but contain an interior nucleus of calcium carbonate. This fact suggests that these phosphates owe their origin to an infiltration of soluble phosphate into calcareous rock. At Safaga and Kosseir, on the Red Sea, and at Sebaia, on the Nile, there are deposits which after concentration yield products with from 60 % to 70 % phosphate of lime and 1 % to 3 % oxide of iron and alumina.

South Africa contains low-grade deposits of phosphate rock at Saldanha Bay, just north of Cape Town. Much of the material is sent to the Transvaal where the need for phosphates is very great. It is estimated that 2000–3000 tons a month will be turned out before long. In South West Africa there are some smaller deposits at Cape Cross which are now available.

Table 6 has been taken from Ulman and Fritsch and revised and added to for the purpose of this volume. It gives a fairly complete list of the most important phosphatic deposits, with some notes on their composition.

TABLE 6.

PRINCIPAL PHOSPHATE

Geographical Distribution and Chemical Composition

Localities.	Designation.	Water.	Loss on ignition.	Lime.	Oxide of iron.	Alumina.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Sweden and Norway.						
Krageroe	Apatite	0·45	—	45·58	1·00	0·77
Langesund	Chlorapatite	0·32	—	51·02	0·90	—
Germany.						
Hartz	Apatite	1·2	—	—	2·4	
Helmstedt	Phosphorite	4·2	—	—	2·86	—
Wasserleben	,,	6	—	—	1·72	—
Lahn et Dill	,,	3·85	—	37·31	4·75	3·08
Peine	Coprolites	—	—	—	Very rich in iron	
Horde	Phosphorite	—	—	—	Up to 19 % of iron	
Amberg	Osteolite	—	—	—	—	—
Delme (Lorraine)		—	—	—	Oxides of iron and alumina 8–12 %	
Austria-Hungary.						
Schlaggenwald (Bohemia)	Apatite	—	—	—	—	—
Lavanthal (Carinthia)	Phosphorite	—	—	—	—	—
Starkenbach (Bohemia)	Coprolites	—	74·03	12·26	—	—
Cracow (Galicia)	Bat guano	7·50	75·20	—	—	—
Belgium.						
Liège	Phosphatic chalk	0·93	2·83	40·64	2·39	
Ciply	,, ,,	1·52	—	45·45	1·75	1·11
		3·60		50·55	1·09	
France.						
Bellegarde-sur-Rhone	Coprolites	4·70	0·2	32·50	16·90	—
Somme	Phosphorite	1·69	—	47·34	2·21	
Lot	,,	4·27	—	50·10	2·96	
Vaucluse	,,	2·45	—	26·57	3.30	
Ardennes	,,	—	—	—	4·6	2·3
Boulogne	Coprolites	0·84	3·14	33·06	2·89	3·09
Italy.						
Sardinia (Cagliari)	Bat guano	18·77	6·14	5·17	trace	trace

DEPOSITS.

of Deposits of Phosphate of Lime and Guano.

Magnesia.	Phosphoric acid.	Nitrogen.	Tribasic phosphate of lime.	Carbonate of lime.	Calcium fluoride.	Analyst.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
—	34·30	—	74·87	—	—	A. Retter.
0·80	38·02	—	82·99	—	—	E. Gussefeld.
—	18·32	—	35·45	7·10	—	
—	19·27	—	41·48	8·9	—	
—	18·18	—	39·70	7·9	—	E. Schulte.
0·18	29·19	—	63·72	—	15	Dietrich and Konig.
—	34·35	—	74·88	—	—	
—	19·52	—	44·20	—	—	
—	36·64	—	80	—	3·0	
—	18·04	—	33·44	—	—	
—	30·59	—	66·79	8·54	5·26	Meusel.
—	29·30	—	64·39	13·5	—	
1·31	6·99	—	15·25	—	—	Reuss.
—	3·82	9·17	83·3	—	—	Scheibler.
0·79	27·25	—	59·49	7·04	—	Anglo-Cont. G. W.
—	22·17	—	48·44	—	—	A. Grimm.
1·14	19·80	—	—	39·18	—	Robertson.
—	12·12	—	26·40	—	—	Duglere.
0·78	32·25	—	70·42	9·10	—	A. Grimm.
0·26	37·07	—	80·92	3·43	—	Ulex.
0·33	19·90	—	43·44	0·84	—	E. Gussefeld.
—	17·04	—	36·43	10·13	3·0	Delattre.
0·58	21 06	—	45·97	—		
0·86	50·2	5·72	10·95	—	—	Davesi and Rotond.

Localities.	Designation.	Water.	Loss on ignition.	Lime.	Oxide of iron.	Alumina.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Spain.						
Caceres	Phosphate	0·72	—	—	0·91	0·42
Estremadura	Phosphorite	0·30	—	43·41	1·64	
Logrossan	,,	2·40	—	—	2·22	
Truxillo	,,	—	—	—	—	little
Russia.						
Podolia	Phosphorite in balls	—	—	—	—	—
Kursk	,, ,,	3·57	—	—	1·96	—
Woronesch	,, ,,	—	—	—	—	—
Great Britain.						
Ipswich (Suffolk)	Coprolites	—	—	—	5·0	4·0
Cambridge	,,	4·01	—	45·39	1·87	2·57
Bedford	,,	—	—	—	—	—
Wales	,,	1·4	—	23·48	—	—
Lyme Regis	,,		6	—	7·47	5·70
Goodrich	Mineral phosphate	—	—	42·84	2·36	
NORTH AMERICA.						
Canada.						
Ontario	Apatite	0·08	—	—	—	—
Ottawa	,,	—	—	—	0·09	0·57
	,,	—	—	55·45	—	—
United States.						
New York	Apatite Laurenzia	0·2	—	51·48	1·07	
South Carolina	Phosphate	1·56	—	42·28	—	—
Charleston	,,	9·95	6·65	31·12	2·86	2·38
Port Royal	,,	0·58	1·01	37·79	2·82	1·12
Tennessee	,,	0·80	—	50·60	3·32	
Florida	,,	0·55	—	50·46	1·95	
Tallahassee	,, (Hard rock)	0·25	—	—	0·82	1·27
Barlow	,, (Land pebbles)	—	—	—	0·80	1·37
Peace River	,, (River pebbles)	1·05	—	—	0·52	1·64
Pebble		1·46	2·41	47·10	1·60	
WEST INDIES AND MEXICO.						
West Indies.						
Havana	Phosphate	11·90	—	—	2·88	—
Guanahani	Phospho guano	9·83	—	30·60	5·77	
Vivorilla (Isle)	,,	7·0	6·46	45·26	0·25	
Puerto Rico (Ponce)	Bat guano	17·68	51·66	10·17	1·59	
Lesser Antilles.						
(*a*) Windward (Isles).						
Avalo (Isle)	Guano in crusts	20·12	—	31·15	5·88	trace
Navassa (Isle)	Coralline phosphate	2·7	—	37·6	14·8	
Mona (Isle)	Phospho guano	7·66	—	—	0·75	

Magnesia.	Phosphoric acid.	Nitrogen.	Tribasic phosphate of lime.	Carbonate of lime.	Calcium fluoride.	Analyst.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
—	29·46	—	59·59	13·23	0·98	Niederstedt.
—	32·60	—	71·16	—	7·8	A. Grimm.
—	38·95	—	85·03	10·35	—	De Luma.
—	35·50	—	75·80	little	1·40	
—	34·0	—	74·23	6·92	—	
—	35·42	—	77·34	—	—	Schwackhofer.
—	13·74	—	30·0	24	—	Pieper.
—	24·73	—	54·0	10·0	9	Voelcker.
0·48	26·75	—	57·12	—	—	,,
—	18·32	—	40·0	—	—	
—	15·4	—	33·62	—	—	Herepath.
—	27·95	—	6·1	24·0	—	
—	27·63	—	60·32	9·54	—	
—	39·98	—	86·61	4·47	7·22	W. R. Hutton.
0·15	39·0	—	85·24	0·06	6·8	
—	39·49	—	86·09	5·07	—	Robertson.
—	37·0	—	79·59	2·32	6·42	H. Gilbert
—	26·89	—	58·70	—	—	Voelcker.
1·62	20·92	—	45·66	—	15·5	Ulex.
0·5	23·67	—	51·67	9·18	—	
—	36·69	—	80·09	—	—	H. Grimm.
—	35·80	—	78·15	—	—	,,
—	35·42	—	77·32	—	—	Pieper.
—	31·59	—	68·96	—	—	Voelcker.
—	28·08	—	61·30	—	—	Gilbert.
1·90	31·50	—	68·67	6·91	—	Robertson.
—	34·08	—	74·40	—	—	Pieper.
—	11·60	0·73	25·32	—	—	A. Grimm.
1·27	32·24	0·13	70·38	—	—	H. Gilbert.
0·17	7·57	8·35	16·52	—	—	A. Grimm.
0·44	24·36	0·45	53·18	—	—	A. Schlimper.
0·6	33·5	0·11	73·13	5·6	—	Ulbricht.
—	27·85	0·25	60.79	3·80	—	Weiss.

Localities.	Designation.	Water.	Loss on ignition.	Lime.	Oxide of iron.	Alumina.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
(*a*) Windward (Isles)	—*contd.*					
Sombrero (Isle)	Guano in crusts	9·06	—	36·17	2·42	6·89
St. Martin (Isle)	Mineral phosphate	5·04	—	47·69	1·21	2·99
Redonda (Isle)	Phosphate of alumina	23·23	—	—	36·38	
Alta Vela	,, ,,	16·49	—	—	19·24	
Lower Antilles.						
(*b*) Leeward (Isles)						
Aruba (Isle)	Mineral phosphate	3·46	—	48·72	3·25	
,,	,,	2·16	—	47·84	1·36	0·61
Curacao (Isle)	,,	0·84	—	51·00	0·2	—
Buenos Aires (Isle)	,,	20·0	—	—	—	—
Los Aves (Isle)	Phospho guano	5·93	—	37·92	1·02	
,,	,,	10·35	—	—	0·16	—
,,	,,	14·90	—	—	0·35	
Los Roques (Isle)	Guano in crusts	10·22		38·67	0·40	—
,,	Phosphate of iron	—	—	—	40·05	
Testigos Isle	,,	12·17		0·37	13·30	—
Mexico.						
George (Isle)	Phospho guano	—	—	—	1·50	—
Raza (Isle of)	,,	4·08	—	35·28	1·14	—
Clipperton (Isle)	,,	3·80	4·83	49·25	0·04	0·04
SOUTH AMERICA.						
Venezuela.						
Maracaibo (Monkey Island)	Phospho guano	2·38	—	39·48	—	—
Brasil.						
Fernando Noronha (Isle of Rata)	Phosphate	10·0	—	30·6	9·56	11
Patagonia.						
East Coast	Guano	16·15	28·06	20·20	0·99	
Falkland (Isle)	,,	8·86	17·10	—	—	—
Peru.						
Lobos de Tierra (Isle)	Guano	23·79	—	18·91	1·89	
Lobos de Afuera (Isle)	,,	19·60	—	—	—	—
Macabi ,, (Isle)	,,	30·33	—	—	—	—
Guanape ,, (Isle)	,,	25·88	—	—	—	—
Chinchas (Isle)	,,	—	—	10·99	0·30	—
Ballestas (Isle)	,,	14·87	—	—	—	—
Independencia Bay	,,	13·22	—	12·59	1·52	1·52
Chili.						
Pabellon de Pica	Guano	13·05	—	14·23	2·73	
Punta de Lobos	,,	14·12	—	—	—	—
Huanillos	,,	14·12	—	—	—	—

Magnesia.	Phosphoric acid.	Nitrogen.	Tribasic phosphate of lime.	Carbonate of lime.	Calcium fluoride.	Analyst.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
0·36	34·41	—	74·55	—	—	Voelcker.
0·38	24·14	—	52·70	32·27	—	,,
—	36·95	—	80·66	—	—	,,
—	20·45	—	44·64	—	—	,,
—	36·29	—	79·22	—	—	E. Gussefeld.
trace	33·82	—	71·65	10·66	—	A. Retter.
0·97	39·96	—	87·23	6·99	1·5	E. Gussefeld.
—	21·76	—	45·50	—	—	,,
—	26·32	0·36	57·45	—	—	A. Grimm.
—	29·02	—	63·37	12·83	—	
—	22·40	—	48·90	7·05	—	
2·75	40·49	—	60·80	—	—	Taylor.
—	37·0	—	80·77	1·0	—	Schucht.
0·57	17·41	—	38·0	—	—	Ure and Teschenmacher.
—	37·71	—	82·33	—	—	E. Gussefeld.
1·18	39·70	0·40	86·66	—	—	Fr. Voigt.
0·25	36·07	0·06	78·84	6·72	—	H. Gilbert.
1·17	41·34	0·14	90·24	—	—	Voelcker.
—	26·5	—	—	—	—	Schucht.
—	15·43	4·40	33·68	—	—	A. Grimm.
—	9·75	1·24	21·29	14·02	—	Anderson.
0·27	17·54	5·58	38·24	—	These guanos contain potash	Anglo-Cont. G. W.
—	16·70	3·60	36·41	—		,,
—	11·95	11·05	25·05	—		,,
—	12·25	11·0	26·70	—		,,
1·19	13·52	14·39	29·47	—		,,
—	12·23	12·50	26·68	—		,,
0·39	10·89	7·68	23·74	—		,,
0·20	12·78	8·88	27·86	—		,,
—	15·10	5·70	32·91	—		,,
—	13·30	6·60	28·99	—		,,

Localities.	Designation.	Water.	Loss on ignition.	Lime.	Oxide of iron.	Alumina.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Chili—*contd.*						
Mejillones	Phospho guano	4·44	—	37·64	0·66	0·90
Angamos	Guano	7·39	64·81	5·11	0·88	
Corcovado	,,	18·19	—	13·67	0·20	
OCEANIA.						
Sporadic Isles.						
Fanning (Isle)	Phospho guano	8·00	12·32	42·84	—	—
Jarvis (Isle)	,,	12·12	5·10	34·83	0·09	—
Malden (Isle)	,,	4·78	5·18	46·23	—	—
Starbuck (Isle)	Guano in crusts	10·01		44·96	—	—
Makatea	,,	1·46	3·39	52·38	1·01	
Phœnix Group of Isles.						
Mary (Isle)	Phospho guano	5·63	—	44·40	0·23	
Enderbury (Isle)	,,	8·76	8·81	40·76	—	—
Phœnix (Isle)	,,	4·93	8·66	44·91	0·23	
Sidney (Isle)	,,	7·38	7·59	42·96	—	—
Gilbert Group of Isles.						
Ocean (Isle)	Phosphate	1·01	2·7	49·5	0·42	
Baker Isles.						
	Phospho guano	3·95	7·76	43·38	0·07	—
Howland (Isle)	,,	5·34	—	44·48	0·18	
Australian Continent.						
Shark's Bay	Phospho guano	15	—	—	—	—
Australian Isles.						
Brown (Isle)	Phospho guano	15·00	10·30	39·94	0·32	—
Jones (Isle)	,,	7·93	10·92	42·86	0·33	0·54
Lacapedes (Isle)	,,	6·78	10·54	41·33	1·61	—
Abrolhos (Isle)	,,	4·48	—	43·20	3·10	
,,	,,	10·10	6·20	—	1·67	
Huon (Isle)	,,	9·74	19·90	37·60	0·24	—
Bird's (Isle)	,,	10·70	9·70	—	—	—
Bat (Isle)	Guano	14·53	—	14·64	0·40	0·57
ASIA.						
Palestine.						
Country East of Jordan	Phosphorite	—	—	—	0·64	0·48
Arabia.						
Kurian Murian (Isle)	Phospho guano	8·70	9·30	—	—	—
Malay Archipelago.						
Timor (Isle)	Phospho guano	6·25	—	40·33	1·48	
Christmas (Isle)	Phosphate	3·05	—	—	0·71	1·22

Magnesia.	Phosphoric acid.	Nitrogen.	Tribasic phosphate of lime.	Carbonate of lime.	Calcium fluoride.	Analyst.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
2·90	31·72	0·59	69·24	—	—	A. Grimm.
1·11	7·13	19·28	15·54	—	—	Anderson.
1·17	15·14	10·52	33·00	—	—	Anglo-Cont. G. W.
0·61	34·16	—	74·57	—	3	H. Gilbert.
0·57	17·67	0·65	38·57	—	—	V. Liebig.
—	34·75	—	75·86	8·29	—	Voelcker.
—	40·12	—	87·58	—	—	,,
1.35	38·24	—	83·36	3·85	—	Robertson.
—	29·26	0·54	63·87	—	—	A. Grimm.
—	28·74	0·38	62·74	16·50	—	Voelcker.
—	36·10	0·63	70·80	4·54	—	
2·3	34·41	0·28	75·13	6·0	0·82	H. Gilbert.
—	38·73	—	84·65	4·91	1·0	V. Gruber.
2·21	40·33	1·35	88·03	—	—	V. Liebig.
—	29·75	0·53	69·94	—	—	A. Grimm.
—	23·59	—	50·53	4·6	—	
0·21	31·40	—	68·54	—	1	H. Gilbert
—	34·22	—	74·70	4·25	—	A. Grimm.
0·55	35·22	—	76·88	—	traces	Cherson.
—	—	0·38	69·46	—	—	A. Grimm.
0·97	33·67	—	70·32	—	7·8	H. Gilbert.
0·09	28·59	1·16	62·41	—	—	Chevron.
—	—	1·24	23·15	36·45	—	Anderson.
—	7·30	7·54	15·94	6·97	—	Voelcker.
traces	38·24	—	83·68	—	9·8	Elschner.
—	26·24	1·37	57·30	—	—	Huson.
—	31·14	0·82	67·98	6·23	—	A. Grimm.
0·26	39·18	—	83·53	4·82	3·44	H. Gilbert

Localities.	Designation.	Water.	Loss on ignition.	Lime.	Oxide of iron.	Alumina.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
AFRICA.						
North Africa.						
Algeria	Mineral phosphate	2·39	—	50·10	0·53	
,,	,,	3·26	4·39	43·30	4·98	
Tebessa	,,	1·97	—	50·30	0·55	
Toqueville	,,	0·77	—	—	0·98	
Tunis	,,	5·95		45·35	0·81	0·62
,,	,,	9·98	3·21	48·40	4·34	
Sfax	,,	—	—	—	1·2	0·6
Gafsa	Phosphate	2·6	2·99	45·12	1·68	
,,	,,	0·72	3·28	46·13	2·59	
Egypt	Bat guano	17·19	29·50	—	—	—
,, Kosseir, Red Sea	Mineral phosphate	—	—	—	1·5	
,, Safaga, Red Sea	,,	—	—	—	2·7	
,, Sebaia	,,	—	—	—	3	
South Africa.						
Damaraland	Guano	18·89	—	12.42	—	—
Ichaboe (Isle)	,,	17·97	17·0	—	—	—
Saldanha Bay	,,	17·04	—	24·26	2·27	
,,	,,	—	—	—	—	—
Algoa Bay	Phospho guano	20·25	12·10	—	—	—

The Operation of Grinding Phosphates.—Rock phosphates are ground in a crusher, and riddled by cylindrical rotary screens similar to those used for the manufacture of road metal. After having been reduced to gravel by such a process, the phosphates are ground in a roller or ball mill. A popular kind of mill for this purpose is a ball mill, which contains from one to five balls of 1 cwt. each (see p. 137). The so-called balls are very frequently of ring shape, running in a groove. For some purposes disintegrators are used, in which four or more arms dash the material against a corrugated side, by which the lumps of phosphate become broken into small pieces or dust (see p. 116). Whether a ball mill or disintegrator be used, the fine dust is blown through screens by a draught of air from a fan, until all the material passes through a sieve containing 60 meshes to the linear inch. Of the powder so produced, nearly 92 %

Magnesia.	Phosphoric acid.	Nitrogen.	Tribasic phosphate of lime.	Carbonate of lime.	Calcium fluoride.	Analyst.
Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
—	30·44	—	66·45	—	—	A. Grimm.
1·72	25·35	—	55·26	12·50	—	Robertson.
0·50	28·16	—	61·47	20·19	—	A. Retter.
0·81	26·32	—	57·46	22·80	—	,,
0·6	27·25	—	59·48	11·52	—	Schucht.
0·90	26·13	—	56·96	21·10	—	Robertson.
—	27·2	—	59.0	14·0	—	,,
0·5	27·23	—	59·44	11·95	—	Schucht.
2·02	27·27	—	59·45	15·20	—	Robertson.
—	—	11·81	—	—	—	Voelcker.
—	—	—	70	—	—	
—	—	—	64	—	—	
—	—	—	60	—	—	
—	13·40	8·88	29·25	—	—	A. Grimm.
—	11·19	—	24·44	—	—	Anderson.
0·97	24·52	1·41	55·40	—	—	H. Gilbert.
—	15	—	33	—	—	
—	6·68	0·43	14·60	—	—	Grouven.

will, as a rule, pass through a standard basic slag sieve containing 100 meshes to the linear inch. In the gravel condition rock phosphates are far too insoluble for manures, but when ground up to the degree of fineness stated above, they can be used directly for this purpose, and have been used very successfully in applications to grazing land or permanent hay. Some records of their having been used successfully for turnips may also be found, but general experience has shown some doubt about the advisability of using rock phosphates for the more intensive forms of cultivation unless accompanied by water soluble phosphate. In practice, rock phosphates are always slow in their action, though in the case of permanent pasture this may be of no great importance. The delay in obtaining a profitable increase from the use of insoluble phosphates may be compensated for by the greater economy of the material. For

most agricultural purposes it is found advisable to treat rock phosphates with sulphuric acid for the manufacture of superphosphate, as described on p. 128.

Potash Mines

German Deposits.—In prospecting for sources of common salt, some mines near Stassfurt were found, about 1850, to contain deposits of potash suitable for use as fertilizers. At first the mines were chiefly worked for the production of common salt, but at a later date the value of the potash produced exceeded that of the sodium chloride raised. The amount of potash contained in the different deposits varies considerably from place to place. The richest crude salt is sylvinite, which consists of magnesium and potassium chlorides, but the deposits in Northern Germany yield little sylvinite. Pure sylvinite contains 26·3 % of potassium chloride. The next in order of importance among these minerals is pure kainite, a mixed salt containing potassium chloride and magnesium sulphate, with 26·6 % of potassium chloride. Hartsaltz contains 21·2 % of potassium chloride. Carnallite, composed of the chlorides of potassium and magnesium, has 15·5 % of potassium chloride. Polyhalite contains potassium, magnesium and calcium sulphates. Owing to the large proportion of magnesium compounds which most of the deposits contain, considerable purification must be carried out before pure potassium salts can be obtained, but much of the crude salt has been graded so as to contain 12½ % of K_2O, the other ingredients being mostly common salt and magnesium compounds.

French Deposits.—Mines in Alsace are richer than those in Stassfurt, Alsace mines averaging 22 % potash, against 12 % at Stassfurt. German control has, however, checked the development of the former, to prevent competition with the older Stassfurt workings. The Alsace potash beds, which are only now being fully exploited for the first time, show that they extend over a fairly wide area. The centre of these is in the Mühlhausen district, and the deposits extend to a depth of 1000 metres, but, being nearly level,

are easier to work than some of the German deposits. The percentage of potash is also satisfactorily high. Under French control the Alsace-Lorraine deposits are yielding kainite and sylvinite containing 14 % of pure potash, potash manure salts containing 20 % of pure potash and muriate of potash containing 50 % to 60 % of pure potash.

Other European Deposits.—Galicia contains some small beds not used for export. Some Spanish deposits at Suria, in Catalonia, have recently been discovered in districts where rock-salt mines are already working. For some time German control succeeded in checking the development of these deposits, but there is considerable hope that they will now be pushed ahead. Carnallite and sylvinite are both common in the Spanish deposits. Some of these newer workings are carried down to a depth of 800 metres. Probably these Spanish deposits extend over a large area.

In addition there are the Italian deposits at Erythrea, which are of recent lake formation. The reserves are not very large, but they are extremely rich, some samples containing as much as 80 % of potassium chloride.

United States Deposits.—The United States deposits are salt lakes situated in the Rocky Mountains. The lake Serles, in California, yields liquors which by concentration and crystallization produce potash salts.

African Deposits.—In Tunis there is a salt lake which yields potash and bromine.

Other Sources.—In Chili, in the province of Tarapaca, there are lakes which contain deposits of potassium chloride varying from 3 % to 30 %. Potash, in the form of potassium nitrate, in India has already been alluded to on p. 25. Most of the potash deposits described above have been originally formed in Nature by the evaporation of sea water. When sea water is evaporated, it first deposits sodium chloride and then magnesium salts separate out. This process can be carried out artificially as well as under natural conditions; the employment of fuel, is, of course, out of the question, but sun heat can be utilized under

workable conditions. Sea water is concentrated in lagoons by sun heat, so that during the day the water deposits salt, mixed with a little magnesium sulphate. During the night it cools to such an extent that magnesium sulphate crystallizes out, and the density of the liquor falls. Next day, when the water again becomes heated by the sun, the salt deposited does not dissolve, but the layer of magnesium sulphate is covered by a fresh deposit of mixed salts; this deposition of alternate layers continues until the mother liquors are sufficiently concentrated. The liquors are removed to large tanks and refrigerated, when Carnallite, a crystalline compound containing potassium and magnesium chlorides, separates out. By treating Carnallite with a little water, most of the magnesium chloride can be dissolved, leaving a product containing about 75 % of potassium chloride. The magnesium compounds are returned to the lagoons, so as to hasten a fresh crop of carnallite crystals. Japan produces 240,000 tons of bittern from the mother liquors of salt pans. This mother liquor contains 68 % of water, and nearly ½ % of potassium chloride. Of the potassium present, 80 % can be recovered as an 80 % potassium chloride. Sicily produces about one-half as much bittern as Japan.

Table 7 gives the amount of potash in different kinds of salt water.

TABLE 7.

USEFUL SALTS IN SEA WATER.

Locality.	Red Sea.	Dead Sea.	Ocean.
Sp. gr.	1·03060	1·1	1·024
NaCl, per million ..	30,000	108,630	25,000
KCl	2,880	13,468	—
K_2SO_4..	2,950	—.	13,000

Attempts to utilize other minerals containing potassium have not, up to the present, been very satisfactory. Felspar, on heating in a furnace with lime and other substances, can be made to yield a considerable quantity of potassium, but the expense is high, and the by-products are very bulky.

As by-products of some other industries, such sources may be useful (see p. 61).

Limestone Formations.—Limestone rocks consist chiefly of calcium carbonate. Chalk is a white limestone, usually soft, containing sometimes as much as 90 % to 98 % of calcium carbonate. Limestones containing a large amount of silica are too dilute for agricultural purposes. Nearly all limestones contain some carbonate of magnesia, those containing a high percentage being called magnesium limestones or dolomites. The limestones belonging to the mountain limestone series are usually comparatively free from magnesia, whereas those of the Permian or magnesium limestone series as a rule contain much magnesia. Even in the Permian series there are large pockets of limestone containing little magnesia and 98 % of calcium carbonate. In the absence of an actual analysis of the product of the quarry a knowledge only of the geological formation may be misleading.

Limestones can be ground in ball mills to a fair degree of fineness (see p. 13). For fertilizers it is quite sufficient to grind the limestone fine enough to be able to pass a sieve containing 50 meshes to the linear inch; finer grinding is much more expensive with little corresponding advantage. Ground limestone is very suitable for direct application to the land, but the greater part of the limestone quarried is generally converted into lime by burning. The tension of decomposition of calcium carbonate approaches that of atmospheric pressure when the temperature exceeds 800° C., but in practice the temperature for burning lime is markedly higher. When it is of little consequence if the mineral matter of the fuel become mixed with the resulting lime, fuel and limestone are mixed together. Where it is desirable to keep the non-calcareous matter low, efforts are made to keep the two ingredients separate, but for agricultural purposes the presence of a small amount of silica is perfectly harmless. It is, however, essential that the limestone used in the kiln should be of good quality, and contain a high percentage of calcium carbonate, otherwise the resulting

lime is so diluted that the cost of carriage becomes prohibitive. Lime kilns can be built on the sloping side of a hill, on which an arch of large limestones is constructed to act as a fireplace for the fuel. The remainder of the kiln space is occupied with a mixture of limestone and fuel. Continuous lime kilns are also used, the fuel being charged in at the top and withdrawn at the bottom. In some of the best works the fuel is chiefly fed down the side of the furnace, so as to avoid mixture with the limestone ; by these means two grades are produced, one pure lime, and the other lime and fuel ash mixed together. Where lime is required for the manufacture of calcium cyanamide, as in the United States Government nitrate plant at Muscle Shoals, Alabama, lime kilns of a rotary form are employed. They are of steel, lined with firebrick, 125 ft. long by 8 ft. diameter, and rotate once in two minutes on an axis inclined three degrees to the horizontal. The limestone is fed into the upper end while a blast of coal dust and air is forced into the lower end. The temperature averages 900° C. and conversion is complete in four hours. The daily consumption is 200 tons of limestone.

For agricultural purposes lime may be ground in a ball mill to a fair degree of fineness, and bagged and sold as ground lime ; or the lime may be sold as shell lime, or made into slaked lime and sold in that form. All these various forms of lime have their respective advantages for agricultural purposes. Ground limestone will not injure the foliage of any plant, and can be applied at any time to a crop ; on the other hand, ground lime is very active, and is apt to injure foliage, and should, therefore, be only applied either at a time when little vegetation is present or before any seeds are sown. Shell lime has the disadvantage that it is difficult to distribute well, consequently the lumps do not become mixed with the soil for many years. Slaked lime has the advantage that it is a fine, dry powder, easily distributed, that it is not so burning as ground lime, though it is more chemically active than ground limestone. The question of freight must influence the choice that is made

between these various forms of lime since the cost of carriage by rail and cart may easily equal the cost of the material at the kiln. Table 8 gives the composition of lime from a few special sources.

TABLE 8.

COMPOSITION OF LIME.

	Lime.	Magnesia.	Silica.
Northumberland mountain limestone ..	83	0·2	1
" " " ..	81	6	3
Durham, good pocket	90	2	1
Durham magnesium limestone	61	33	1
Ashby	46	23	10
Buxton	98	0.5	—

The limestone in County Durham, being situated on the Permian series, exhibits a great variation in the amount of magnesia. Limestone and lime containing a large percentage of magnesia are not suitable for agricultural purposes. There is much evidence of a negative character to show that magnesium limestones are not harmful, but a few positive results which show harm are quite sufficient to justify the fears, which most farmers have, of such materials.

Gypsum.—Gypsum is derived chiefly through the deposition of calcium sulphate from salt water, in which case the gypsum will contain a certain amount of common salt. Gypsum may be derived from the action of sulphuric acid penetrating limestone and converting the latter into calcium sulphate; with this origin calcium carbonate may be present as an impurity. The sulphuric acid responsible for this conversion may have been derived from pyrites, after oxidation, or even from the decomposition of organic sulphur compounds. Gypsum occurs in many parts of the world, and is comparatively easily mined. The bulk of the gypsum mined in England is contributed by Nottingham. Nova Scotia is also a large producer. A typical gypsum contains about 90 % to 95 % of crystallized calcium sulphate, and 3 % to 5 % of calcium carbonate, with 1 % or 2 % of silica. Some deposits of gypsum contain a little anhydrite,

so that they show a theoretical percentage of more than 100 % of gypsum.

The alkali soils of the United States and the usar soils of India have been ameliorated by the addition of gypsum, but the cost is somewhat great. Gypsum is rarely used directly as a manure in Great Britain, because so much calcium sulphate is applied in the form of superphosphate; in addition to which, in the vicinity of large towns, there is a considerable quantity of sulphuric acid coming down with the rain, so that sulphur compounds need not be used as manure; there are, however, many instances of benefits resulting from the agricultural use of gypsum. Gypsum is used in the fertilizer industry to dry superphosphate; it is sometimes much appreciated by horticulturists, as it helps to overcome the injury done to the soil by excessive applications of sodium salts, introduced as nitrate of soda, common salt and sodium carbonate.

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Section II.—FUEL BY-PRODUCTS

Ammonia.—The commercial distillation of coal began when William Murdock invented his process for obtaining illumination by the combustion of coal gas. When coal is subjected to dry distillation in a closed retort, a complex series of changes take place, the nature of which depends very largely on the temperature of distillation. When the temperature is only just above that at which decomposition begins, the condensible volatile products of distillation consist chiefly of liquids resembling those contained in petroleum oil, whilst the gases that are formed are small in volume. When the temperature is raised, these products undergo further changes, owing to contact with red-hot coke and with the heated surface of the retort, and also by the action of radiant heat inside the retort; these decompositions produce hydrogen, methane, ethylene, benzene, and complex hydrocarbons. By still further raising the temperature the quantity of hydrogen is increased, but the amounts of the complex substances are decreased. Doubtless, in the limit of ascending temperature, nothing but carbon and hydrogen would be produced. The nitrogen is partly retained by the coke, and partly distilled as pyridine and ammonia. In addition, free nitrogen and traces of hydrocyanic acid are produced and mixed with the gas. About 70 % of the coal remains behind in the retort as coke, which, whilst it consists chiefly of carbon, contains also all the mineral matter of the coal and a fraction of the other elements.

When the primary object of the distillation of coal is to produce illuminating gas, there are some slight differences of procedure from when the primary object is the production of coke for iron smelting. The horizontal gas retort is

generally made of fire-clay with a section approximating that of the letter " D," the front of the " D " being the base, and the section rather more flattened than the ordinary capital " D " of this type. Sometimes the retorts are permanently closed at one end, when they are usually about 8 or 10 ft. long, but more commonly they are of double length, and open at each end. The end is closed by an iron door, from which ascends a wide pipe, conveying the products of distillation. Firing is frequently done in a modern gas house with producer or water gas. By setting the retort at a sharp angle, or even vertically, much economy in machinery is obtained. The retorts are usually heated for gas production to a temperature of from 900°–1000° C., (1650°–1800° F.), the time of distillation being from 4–8 hours. With vertical retorts, gravity causes the charge to fall, but additional force is supplied by a screw at the bottom and intermittent poking at the top. The volatile products pass through the ascension pipe into the hydraulic main, which latter consists of a long, horizontal tube, traversing the entire length of the retort house. In its passage through these pipes, the gas undergoes rapid cooling and deposits its tar and water, the latter of which absorbs the ammonia, together with a certain amount of hydrogen sulphide and carbon dioxide. The products after leaving the hydraulic main have fallen in temperature to about 50° C., and thence proceed to a condenser, which usually consists of vertical air-cooled pipes, though in some works these pipes are externally cooled by water sprays. The gas, now freed from much condensable material, passes through the exhaust fan, which draws the gas, as fast as it is made, from the retorts through the condensers, maintaining a slight vacuum in these, and then forces the gas forward under pressure through the purifying plant. The first part of the purifying plant consists generally of scrubbers, which are tall towers filled with wooden boards standing on edge, down which water flows. The Livesey scrubber, in which the gas is divided very minutely, and rotary mechanical scrubbers are also used. By these means all the ammonia,

and part of the hydrogen sulphide and carbon dioxide, are washed out of the gas. The ammonia liquor collected from these scrubbers, together with that condensed in the hydraulic main, is drained away into storage tanks, from which it is withdrawn from time to time, to suit the needs of the manufacture of ammonium sulphate or other ammonia compounds which are described on pp. 83 and 89.

When coal is distilled with the object of producing coke, a different quality of coal is frequently used to that which would be suitable for the manufacture of illuminating gas. As it is very necessary that the amount of mineral matter should be reduced, coals are sometimes ground up in mills, and then washed. The washed coal is deposited in special drums and then transferred to a stamping machine, which makes a cake of suitable size for loading into the ovens. The ovens are heated by flues externally. As a rule the coal, whether in washed cakes or in the original lumps, is fed slowly into the top of the horizontal retort, the finished coke being driven out by a ram. The gases evolved are drawn through scrubbers, which wash out the ammonia. In coke works the methods are very similar to those adopted in gas works, the chief difference being due to the nature of the ultimate products. In the patent recovery oven, the quantity of coal dealt with in a charge is as much as 6 tons; very much larger than that in a gasworks. The temperature of carbonization is probably higher in coke ovens than in gas retorts, but as the gas is of less importance, the precautions needed to prevent admission of air by leakage are regarded less seriously. The common type of oven in general use is a rectangular chamber, which is fired by gas burnt in large Bunsen burners, the gas used being that produced by the ovens themselves. The gases are led off by an ascension pipe into the gas main through exhaust fans, drawn through air and water coolers, and then forced through scrubbers as described above for illuminating gas works. The gas is then returned to the oven for the purpose of providing the heat necessary for distillation.

When the temperature of distillation is low, the gas given off is poor in hydrogen, but rich in hydrocarbons of high illuminating power. As coking proceeds, the ovens become hotter, the gas loses illuminating power, the percentage of hydrogen steadily increases, whilst the hydrocarbons decrease in proportion. As the process of coking continues, the ammonia produced in unit time decreases in amount, until 24–39 hours after starting, when it is practically nil. The temperature steadily rises towards the end of the process. Ammonia decomposes on heating, so that if ammonia gas is passed through a tube filled with broken porcelain, at 600° C. (1112° F.), 34 % of the ammonia is decomposed with a slow flow of gas, and 21 % with a rapid flow, whilst at 780° C. (1436° F.) the decomposition is complete. It is necessary, therefore, that the temperature of the top of the oven should be kept as low as possible. As the oven is heated from the side, and charged from the top, this state of affairs is at least approximated to. Decomposition of ammonia may also take place owing to interaction with red-hot carbon, with the ultimate production of ammonium cyanide. By estimating the quantity of cyanide in the liquors, the amount of hydrocyanic acid produced per 100 parts of ammonia is found to be under 2 parts at about 540° C. (1000° F.), and about 2¾ parts at 560° C. (1200° F.). In the horizontal gas retort there is a comparatively small retort, heated all round by the flue gases. The coal is charged into this red-hot retort, lies in a thin layer at the bottom, and cools the retort. As distillation proceeds, the temperature of the retort rises, and the gases come into contact with the hot sides and top of the retort. That decomposition undoubtedly takes place is proved by the thick deposits of carbon on the roof of the retort. Towards the end of distillation the charge becomes very hot, further decomposition takes place, and no ammonia is produced.

The use of the vertical gas retort has enabled the gas industry to overcome some of these difficulties. With this type of retort there is an upright cylinder, and the coal is charged from the top. Instead of having a large free

space, the coal practically fills the retort, which is heated from the outside, the heat gradually penetrating to the centre. The gas eventually takes its course to the top of the retort through the comparatively cool central core, whence it immediately enters the ascension pipe at a low temperature, and is drawn off with little direct contact with the highly-heated sides of the retort. An attempt is also made to keep the larger lumps of coal towards the central part, and thus assist the passage of the gas up the cooler regions. The average yield of ammonia from vertical retorts is said to be about 7 lbs. per ton of coal, whereas from horizontal retorts it is only about 5 lbs. per ton, but practical experience of both kinds of retorts places the difference at a slightly lower figure. The by-product recovery coke-oven is a large rectangular chamber, which is almost completely filled with coal, leaving only a very small space at the top for the exit of the gas. This coke-oven, therefore, combines some of the features of both the vertical and horizontal gas retorts. The centre of the charge remains at a comparatively low temperature until the end of the distillation. The temperature of the flues used for heating the retort is usually over 1090° C. (2000° F.), whilst that of the gas leaving the oven is little over 540° C. (1000° F.). A small amount of the gas must come into contact with the hot walls and top of the oven, but owing to the large size of the retort this is only a small fraction. As the result of distillation the nitrogen of the coal is distributed in the following manner: with ordinary illuminating gas retorts 12–17 % is in the form of ammonia, 1–2 % is in the form of cyanides, 45–60 % is left in the coke, and from 4–35 % is evolved in tar and gas. The distribution of the nitrogen in the ammonia liquor is 98 % as ammonia, 1½ % as cyanides, and the rest as sulpho-cyanides and ferro-cyanides. In coke-ovens the distribution of nitrogen is as follows: about 15 % is in the form of ammonia, 1½ % is in the form of cyanides, 45 % is left in the coke and 40 % is given off in the tar and gas. If coal is quickly carbonized a much larger proportion of nitrogen is

retained in the coke than when slow carbonization is permitted. With quick heating of 2 or 3 hours in the laboratory, the amount of nitrogen left in the coke from the same kind of coal is from 60–70 %. When coal is distilled at a very low temperature for the production of coalite, or other similar semi-carbonized coal, the yield of ammonia is smaller than when high temperatures are used as in gas or coke production; about 2½ pounds of ammonia per ton of coal when partially distilled as against about 5 pounds when fully carbonized. The presence of air in the retort results in loss of ammonia by oxidation. Steam and hydrogen sulphide conserve ammonia from oxidation in the retorts. At temperatures below 150° C. (300° F.) the oxidation of ammonia by air is negligible.

"Mond" Gas.—In the manufacture of Mond gas the difficulty of using bituminous fuel for the production of water gas has been removed. By blowing a large amount of steam, with the amount of air necessary to produce gas through coal undergoing combustion, the temperature of the gas is kept sufficiently low to enable the major part of the nitrogen in the coal to be obtained as ammonia. For every ton of coal distilled, 2½ tons of steam are admitted. In this process common bituminous slack is first fed into a hopper at the top of a gas generator, where it undergoes distillation, and the volatile products pass down through the hot coal before joining the bulk of the gas leaving the producer. By these means the tar is largely converted into permanent gas, and the partly carbonized slack then passes from the hopper into the body of the producer, where it is acted upon by an air blast, which is saturated with steam at 85° C. (185° F.) and superheated by waste heat from the producer. The bottom of the generator is conical, and is sealed in a tank of water used to receive the ashes, which can be periodically removed without interrupting the manufacture of gas. The hot gases, mixed with excess of steam, leave the generator, and then pass through a heat interchanger, parting with their heat to the air supply of the generator and becoming themselves cooled in the process.

The gas is then passed through a washer, where it is both purified and cooled, and is then generally passed straight into the acid absorber to produce sulphate of ammonia directly. The Mond gas method exceeds all others for efficiency in converting the nitrogen of coal into ammonia.

The Distillation of Peat.—The problem of drying peat has attracted much attention, but the great difficulty in the economic utilization of this material has always been its high percentage of water which amounts on the average to about 90 %. The removal of a portion of this water is comparatively simple, but to reduce the peat to a useful dry commodity is a long and expensive process. Newer processes have shown, however, that it is possible to distil peat which contains about two-thirds of its weight of water, under which circumstances the yield of ammonia is especially high. The Woltereck process claims to produce 30 lbs. of ammonia per ton of dry peat, or per 3 tons of peat of the degree of wetness which can be used in that plant.

Gas Lime.—After the removal of ammonia in the process of making gas from coal, the gas still contains as impurities hydrogen sulphide, carbon dioxide and carbon disulphide, as well as thiophene and other organic sulphur compounds. When no effort is made to purify the gas beyond removing hydrogen sulphide, the iron oxide method of purification is adopted, but when an effort is made to remove carbon disulphide and carbon dioxide, the gas is passed through purifiers, consisting of large cast-iron boxes containing layers or wooden grids, on which is placed slaked lime. These boxes are made gas-tight either by a rubber joint or a water lute. As a rule, there are at least three or four boxes, and when the gas enters the first, the carbon dioxide and hydrogen sulphide are quickly absorbed, and then the carbon disulphide combines with the calcium sulphide first produced, forming calcium thio-carbonate. These reactions are explained in the equations—

(1) $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$
(2) $Ca(OH)_2 + H_2S = CaS + 2H_2O$
(3) $CaS + CS_2 = CaCS_3$.

After the first box is nearly saturated, the carbon dioxide acts on the calcium sulphide already formed, giving free hydrogen sulphide, according to the equation—

$$(4)\quad CaS + H_2O + CO_2 = CaCO_3 + H_2S.$$

The first box is now removed from action, so that the second box becomes the first box, the third the second, and so on, and a new box is put on at the end of the series; by these means economy in the use of lime is obtained. The spent lime emptied from the boxes has a highly objectionable odour, and has no value apart from its demand for agricultural purposes. Where a small gasworks is situated in an agricultural district, no difficulty occurs in obtaining a sufficient sale for the gas lime, although, in any case, it is not a profitable by-product; where, however, large works are situated in urban areas, it is impracticable to get it all removed to the land, and large quantities are taken and dumped out at sea.

The successful application to the land of gas lime, limestone, chalk and other bulky calcareous substances, depends on a great variety of conditions; but gas lime has a peculiar action, due to the sulphides, sulphites, cyanides and other poisonous compounds contained. In fresh gas lime the proportion of water varies from about 30–40 %. Air soon acts on fresh gas lime; atmospheric carbon dioxide brings equation (4) into play and, similarly acting on calcium thio-carbonate gives rise to carbon disulphide as well; the objectionable odour begins to disappear on storage, since the odorous compounds are oxidized to sulphates and other inoffensive compounds. Fairly old samples of gas lime contain no sulphide of lime, but only sulphite, while the cyanides are converted into Prussian blue. Table 9 indicates the composition of a typical well-weathered gas lime :—

TABLE 9.

COMPOSITION OF GAS LIME (DRIED AT 100° C.) (Voelcker).

Water of combination and a little organic matter ..	7·24
Oxides of iron and alumina, with traces of phosphoric acid	2·49
Sulphate of lime (gypsum)	4·64
Sulphite of lime	15·19
Carbonate of lime	49·40
Caustic lime	18·23
Magnesia and alkalies	2·53
Insoluble siliceous matter	0·28
	100·00

The chief results of applying gas lime to land consist in the beneficial effects produced on the land by the calcium carbonate contained; as with other forms of calcium oxide or carbonate, heavy land is rendered easier to cultivate. There is nearly always a little nitrogen present in gas lime. Where a soil is at all alkaline, the sulphate of lime will be useful. Gas lime is also a means of killing off various pests, such as wire worms, and destroying matted, useless growths of grass of little feeding value. Inferior matted grass on pasture can be removed by substantial dressings of gas lime, as it burns up and destroys much of the rank herbage; although for the next few months the pasture is worthless, it subsequently recovers, and in a few years becomes fine pasture of good feeding value. Other methods of effecting this result are fully described in "Plant Products" (pp. 6, 63, 95). Gas lime is now produced in such relatively small quantities, owing to the introduction of other methods of purification, that the subject of gas lime is of far less importance than it was in former days.

Acetylene Gas By-product.—When calcium carbide is treated with water in the production of acetylene, a residue is left which contains about 50 or 60 % of pure lime. The lime is in the form of calcium hydrate with an excess of water. Traces of undecomposed carbide, phosphide, sulphide and silicide continue to evolve traces of odorous and poisonous gases, but the amount of these impurities is of no practical importance in agriculture. Prudence suggests that an application of such a residue should be early so that

these gases may have time to pass away before the crop begins to grow.

Soot.—Soot has long been known and highly esteemed as a useful manure. It is obtained by the combustion of either coal or wood but the major part of that obtained to-day owes its origin to the combustion of coal. When coal is burnt in a fireplace the greater part burns away, but some portions are only incompletely burnt, and pass up the chimney to form minute particles of smoke. Soot consists of the deposit of these minute particles of carbon, tar, ash and other products of imperfect combustion. Some of the nitrogen in the coal is evolved as ammonia, and much of the sulphur as sulphur dioxide. The two passing together up the chimney, oxidize and condense as ammonium sulphate. Ordinary soot, which is usually acid to litmus, consists mainly of carbon, tar and mineral matter with small quantities of nitrogen and sulphur compounds. Analyses of soot show very great variations in composition, but this is not to be wondered at, considering the great variation of conditions under which coal is burnt. Soot is a product of incomplete combustion, and its composition will therefore depend upon the particular degree of incompleteness with which the fuel has been burnt. The degree of draught up a chimney will also have a powerful influence on the amount of mineral dust carried forward. With the high temperatures and strong draughts of a factory furnace, a large proportion of the soot is produced by the mechanical removal of small particles due to the strong draught; but in the domestic fireplace, where the draught is small, it is the incomplete combustion of the fuel to which must be attributed the larger part of the materials found in the soot. Further, the actual distance from the fire to the place where soot is deposited will cause a great variation in the composition of the soot, since the draught is a cause of the separation of the constituents of the soot and the temperature of the place of deposition will control the proportions of partly volatile substances deposited thereat. Table 10 gives the result of examining soots produced from the same coal under

different conditions, from which it will be noticed that a very great variation in composition exists, due to the methods by which the coal is burnt.

TABLE 10.

ANALYSES OF SOOT (Cohen and Ruston, Leeds).

	Coal.	Domestic soot.	Boiler soot.		
			Base.	70 ft. up.	Top, 110 ft up.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Carbon	69·30	40·50	16·66	21·80	27·00
Hydrogen	4·89	4·37	0·86	1·44	1·68
Nitrogen	1·39	4·09	0·00	1·18	1·21
Ash	8·48	18·16	75·04	66·04	61·80
Tar	1·64	25·91	0·09	0·80	1·66
Sulphur	1·74	2·99	2·07	2·58	2·87
Chlorine	0·27	5·19	0·11	1·46	1·60
Acidity (H_2SO_4) ..	0·00	0·37	1·33	0·58	0·56

Owing to the high velocity of the wind current in the flue from a boiler, the percentage of ash in boiler soot is very high, whilst in the domestic fire grate it is the proportion of tar that is strikingly high. The percentage of nitrogen is much higher in domestic soot than in factory soot, Owing to the high temperatures in the lower portions of the factory chimney, little ammonia is deposited there, but it is condensed higher up the chimney, where lower temperatures prevail. Many varieties of domestic soot contain a higher percentage of nitrogen than the particular specimen analysed for Table 10. Even the soot from a foundry using liquid fuel is not entirely devoid of nitrogen. Considerable variations also occur, even in ordinary domestic soot, between the soot collected from an ordinary open sitting-room fire and that collected from a kitchen range; the percentage of nitrogen in soot from a kitchen range is always lower. In the case of an ordinary sitting-room chimney, the richest soot is deposited comparatively low down, about 5 or 10 ft. from the fire; the soot obtained from regions near the chimney top being of lower nitrogen content. The region in which most of the nitrogen condenses

is one of moderate temperature. With high temperatures and strong draughts the ammonia compounds are carried up the chimney, whilst with lower temperatures they are deposited near the source. It is obvious, therefore, that the point where the major part of the ammonia condenses will vary from hour to hour in the same grate.

Soot, when used as a fertilizer, is a substance of considerable importance, its value being often quite as much due to physical and poisonous properties as to its fertilizing elements. The dark colour of the soot makes it a very effective absorbent of the sun's rays, so that for garden work it is very valuable, as it raises the temperature of the soil 2° or 3° above that of land which has not been darkened in colour; there is no corresponding loss of heat at night by radiation from these darkened soils, since a local mist is produced over the surface at night which prevents further loss. Soot makes a very valuable top dressing for wheat, the accruing benefits being very probably due to its nitrogen content. Soot is also specially distasteful to slugs and small snails, and is largely used by gardeners for that reason. As nearly the whole of the nitrogen in the soot is present as ammonium salts, this fertilizer is a quick-acting one. Soot is very commonly sold by the bushel. The best varieties of soot, as produced in the domestic grate, are much lighter than the poorer varieties from the factory chimney. There is, in fact, a fairly close relationship between the percentage of nitrogen and the weight in pounds per bushel. On the average, a soot containing about 1 % of nitrogen weighs 40 lbs. to the bushel, with 2 % of nitrogen about 33 lbs. per bushel, with 4 % of nitrogen 24 lbs. per bushel, and with 7 % of nitrogen 15 lbs. per bushel.

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Section III.—METAL INDUSTRY BY-PRODUCTS

Blast-Furnace Dust.—The iron industry has, in very recent years, provided a valuable by-product containing much potash. Although the percentage of potassium contained in the compounds charged into the blast furnace is comparatively small, yet an important concentration occurs in the process. In the modern blast furnace, ironstone, limestone and hard coke are charged at intervals, through a closed hopper, into a tall vertical blast furnace. The blast produces such a high temperature that some of the potassium compounds present are volatilized and carried forward into the flues. For the purpose of economizing heat, the waste flue gases are passed through heat-interchanging ovens for the purpose of heating the blast of air, and then pass on to boilers for raising steam. During the passage of the blast-furnace gases through the tubes in ovens or boilers, a fine dust is deposited, which has been found to contain potash in forms easy to concentrate. The potash content of these flue dusts is very variable, the large amount of black dust deposited in the first dust catcher being comparatively poor in potash, but the rather reddish dust deposited in the stoves and boilers contains a larger amount, and the very small yield of light-coloured dust at the base of the chimney stacks is the richest of all. The English type of furnace, fed with coke, produces a larger amount of potash than the coal-fed furnaces used in Scotland. When the blast-furnace gases are cooled by washing with water, much potash is lost in the washing waters since nearly all the potash present in these dusts is soluble in water. Owing to the extremely fine division in which the particles of potash occur, attempts have been made to remove the dust either

by a gas-bag arrangement or by a Cottrell electric dust precipitator; the latter alone is capable of dealing with large amounts of gas. The composition of the dust obtained varies from place to place, a very rich dust showing on analysis 20–25 % of potassium chloride, 15 % of potassium hydrogen carbonate, 5 % of potassium cyanide and small traces of other substances. On the other hand some dusts only contain 1 % of potash. Attempts to raise the amount of potash in the flue dust have been made in a variety of ways, but the most promising of these consists in the addition of a small quantity of common salt, which produces increased volatilization of potassium; very considerable improvements have been made in this way. Experiments made by adding a quantity of salt sufficient to provide chlorine to combine with all the potassium in the blast furnace caused the amount of potash volatilized to be increased three or four times.

The cement industry provides a similar source of potash compounds, but suffers from the difficulty that the cost of collection must be debited exclusively to the potash industry, whereas in the blast-furnace industry the gases must be cleaned and their heat utilized. By the use of salt in the cement kiln, potash in considerable quantities is volatilized into the waste gases. The great difficulty in dealing with this material is the engineering one of providing sufficient plant for the removal of potash fog. The most promising solution of this obstacle is the Cottrell Electrostatic method of recovery (see p. 65). To deal with these materials properly, it would be necessary to erect central potash factories in certain districts. Now that the subject has come under investigation, it is interesting to note the fact that from iron blast furnaces the potash obtained appears to be greater than is accounted for in the charges. The cause of this discrepancy may be that the ordinary methods of estimating potash in these compounds are a little faulty, owing to the fact that in the laboratory some potassium volatilizes during the combustion of the fuel necessary to obtain an ash suited to the subsequent method of analysis. The discrepancy

has also been accounted for by the difficulties of taking samples of blast-furnace charges and products.

Basic Slag.—Whilst the flue gases passing out at the top of the blast furnace contain potash, the phosphorus of the furnace is almost completely removed in the pig iron. Early forms of iron smelting by means of wood charcoal provided a basic ash which prevented the phosphorus from entering the pig iron, but as soon as coal fuel was used and the type of slag in the blast furnace became acid, and not basic, all the phosphorus entered the iron. As phosphorus exceeding 2 % renders iron brittle in the cold, ores containing large amounts of phosphorus were little used until the discovery of methods for removing phosphorus. Phosphorus varies from about 0·02 % in the best Swedish iron to upwards of 3 % in common cinder pig. With ores containing high percentages of phosphorus, a basic process of purification is absolutely essential. In the original process for producing steel from pig iron the vessel was lined with acid materials, but by lining the converters with a basic lining the phosphorus difficulty was overcome. The special lining is manufactured from dolomite, or, at any rate, a magnesium limestone, which is calcined, mixed with tar and made into bricks for lining the furnace. During the process of converting pig iron into steel, lime is usually added, so as to prevent the destruction of the lining, and because the resulting basic slag is better without an excessive quantity of magnesia.

Steel is prepared from pig iron by the Siemens or open-hearth method in increasing quantities to-day; considerable quantities of scrap iron and iron ores are also added in these furnaces. As the temperature of these open-hearth furnaces is lower than that of the converter, a certain amount of calcium fluoride is added to make the slag flow more easily. The open-hearth process differs from the Bessemer converter in that, whilst in the latter the phosphorus remains in the metal until practically all the carbon has been eliminated, in the open-hearth method much of the phosphorus is removed from the metal in the earlier stages of the operation. The open hearth is more easily controlled than the converter,

and permits of the use of large quantities of scrap. In some works the Talbot process of a large tilting furnace of cylindrical form is also used. The resulting basic slag, whatever may be the process of its manufacture, is run out into trucks, cooled and broken up, its subsequent history being described on p. 120. Efforts have been made to improve the quality of the slag from the manurial point of view by adding to it some quantities of rock phosphate. Indian apatite contains too much iron for superphosphate manufacture, but has been used to enrich Indian basic slag which is poor in phosphorus. No doubt this method will increase the percentage of phosphorus in the slag, but whether it is economically justifiable remains yet to be found out.

The Zinc Smelting Industry gives rise to sulphuric acid as a by-product which is used to manufacture superphosphate. The production of sulphuric acid from this source is likely to increase to such an extent as to affect vitally the supplies of superphosphate (see p. 128).

Various small metal industries give rise to by-products of value as fertilizers. Steel cylinders are often annealed and hardened with the aid of powdered charcoal; after a time the charcoal burns away leaving an ash containing potash. Case hardening requires many mixtures containing potassium ferrocyanide, bone meal, etc. The object of such processes is partly physical and partly chemical but they yield residues containing potash, phosphates, etc. Without a knowledge of local customs, the value of such products cannot be gauged.

The Recovery of Nitrogen, Phosphorus and Potassium.—It is interesting to note that by means of the Mond gas process, combined with the blast furnace and basic steel processes, we now possess means for recovering all nitrogen, phosphorus and potassium from any low-grade refuse, and converting them into forms suitable for use as fertilizers. Any refuse, either human, animal, vegetable or mineral, if distilled without previous drying, with steam at moderately high temperatures, will yield almost all its nitrogen as ammonia, and produce a combustible gas. The ammonia

can be converted into sulphate of ammonia, and the combustible gas, together with any coke and lime left, can be added to the blast furnaces, when all the potassium would be volatilized into the blast-furnace gases, to be recovered as flue dust. Most of such miscellaneous refuse would contain sufficient sodium chloride to render all the potassium volatile, but if it did not do so it would be easy to add the necessary chlorides. In addition, the whole of the phosphorus would be concentrated in the pig iron, to be converted into basic slag, in course of time, in the basic open-hearth or Bessemer process. Low-grade basic slags could, as a matter of fact, be returned to the blast furnace when all iron and phosphorus in them would come out with the pig. The next process of purification would therefore produce a richer basic slag, in addition to recovering a good deal of iron which is at present wasted. It would, however, take a good deal of courage and enterprise to initiate any complete process based on such lines.

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Section IV.—ALKALI INDUSTRY BY-PRODUCTS

The Alkali Industry Wastes.—The Leblanc soda industry provides some useful by-products for fertilizing purposes. The Leblanc soda industry consists of two processes: the first is the salt cake process, in which sulphuric acid and sodium chloride are treated together in large cast-iron pots, and the action finished in furnaces. The charge consists of about 16 cwts. of common salt, with 23 gallons of sulphuric acid. As soon as heat is applied, large quantities of hydrochloric acid gas are given off, and the temperature rises. During the first part of the process the reaction that takes place is represented by the equation—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

After the mixture has been heated for about an hour, and the salt has become solid, it is pushed on to the hearth of the furnace. Here the hot air and flame from the fire complete the decomposition between the sodium hydrogen sulphate and the sodium chloride, according to the equation—

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl$$

The resulting material usually contains 95 % of sodium sulphate, with a little sodium hydrogen sulphate, a little sodium chloride and a few impurities introduced accidentally. Muffle furnaces often replace the open furnaces, as condensation of hydrochloric acid is more economically performed when waste fuel gases are not admixed. Mechanical furnaces are also used, which have revolving beds.

After the sodium chloride has been converted into sodium sulphate by the salt cake process, it is then treated by the black ash process, which consists in mixing the salt cake with about its own weight of limestone and rather more than half its weight of coal, the mixture being heated in a

reverberatory furnace. Revolving black ash furnaces are now very largely employed. The first part of the process probably consists in the reduction of sodium sulphate by carbon to sodium sulphide, according to the equation—

$$Na_2SO_4 + 4C = Na_2S + 4CO$$

The second part of the process consists of the conversion of sodium sulphide into sodium carbonate and calcium sulphide by interaction with calcium carbonate, as shown by the equation—

$$Na_2S + CaCO_3 = CaS + Na_2CO_3$$

The soluble products are washed out of the black ash by water, about 48 hours being needed for this washing, and the residue still contains a little sodium carbonate. In modern works much of the sodium carbonate produced is at once converted into caustic soda by boiling with excess of lime, when the changes that occur may be represented by the equation—

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$

Air is blown in to oxidize any iron compounds, which in the ferrous state would remain in solution and contaminate the caustic soda, but which in the ferric state settle to the bottom with the precipitate of calcium carbonate. The calcium carbonate formed in this way is washed free from caustic soda, and, after drying by exposure to air, can be used directly as a lime fertilizer. It consists chiefly of calcium carbonate in a fairly dense condition, and the small amounts of sodium and iron compounds left are of no consequence. The physical condition is good, and the percentage of calcium carbonate about 80 %.

The alkali waste consists of the crude calcium sulphide left as a residue after washing out the sodium carbonate from the black ash; it is now generally used for the recovery of its sulphur. Carbon dioxide from lime kilns, in the form of waste gas, containing about 28 % of carbon dioxide, is forced by powerful pumps through a series of tall closed cylinders containing a cream of alkali waste and water.

At first carbon dioxide is absorbed with the production of calcium carbonate and calcium hydrogen sulphide, the latter being subsequently decomposed by more carbon dioxide, with the formation of more calcium carbonate and hydrogen sulphide. The hydrogen sulphide is removed as gas by the stream of nitrogen left from the kiln gas. The equations which represent these parts of the process are—

(1) $CaS + H_2O + CO_2 = CaCO_3 + Ca(HS)_2$

(2) $Ca(HS)_2 + H_2O + CO_2 = CaCO_3 + 2H_2S$

During equation (1) no hydrogen sulphide is removed as gas and the gas passing away is discharged. During equation (2) the effluent gas contains a much higher percentage of hydrogen sulphide than did the incoming gas contain of carbon dioxide. If the incoming gas contains 20 % of carbon dioxide, the effluent gas contains over 30 % of hydrogen sulphide. The hydrogen sulphide is sometimes burnt to sulphur and water in a special furnace, and sometimes burnt completely to sulphur dioxide, which is then passed through leaden chambers and converted into sulphuric acid. The residual calcium carbonate is run out into heaps, and allowed to dry by drainage and natural wind action. It does not pay to spend any money over this material, but, by merely erecting a few simple sheds to keep off the rain and provide the necessary accommodation for the men employed, a fairly satisfactory form of waste lime can be produced, to be subsequently sold for agricultural purposes under the name of lime mud or Chance mud. This material, as put on the rail in trucks and delivered to the farmer, may contain about two-thirds of its weight of calcium carbonate, the remainder being chiefly water, together with small quantities of calcium sulphate and organic matter, derived originally from the coal used in the black ash process. The material so obtained has the disadvantage that when it becomes thoroughly dry it blows about in the wind. It is therefore best applied to the land in a condition of partial dampness, from 20–30 % of water being a suitable condition for handling. A larger amount of water adds to the weight and makes the material too sticky, but

with much lower proportions of water it becomes too dusty, and blows about with the least wind. The material is so finely divided that it behaves in the soil like clay, and, unless carefully distributed, it may remain in lumps in the soil for years without breaking up; but, being porous, any portions that come near the surface are easily broken up by frost.

Sodium Sulphate.—At Rothamsted this material has been found to have a real fertilizing value; unfortunately, it is not generally considered in the manufacture of fertilizers. It is a product of the alkali industry (see p. 66), and can be obtained readily.

Magnesium Carbonate Wastes.—Magnesium carbonate can be made from the limestone of the Permian series. By Pattinson's process, dolomite, or magnesium limestone, is first of all ignited, and then treated with water and carbon dioxide under pressure. Under these circumstances, the mixed oxides of calcium and magnesium formed on ignition are carbonated, the magnesium carbonate dissolving in the carbonic acid far more readily than calcium carbonate. The solution of magnesium bi-carbonate thus formed is separated from the insoluble calcium carbonate, and subsequently decomposed by a current of steam into insoluble magnesium carbonate and carbon dioxide. The residual calcium carbonate is usually comparatively free from magnesia, and is, therefore, suitable for application to the land. It is rather denser than Chance mud, and is consequently slightly easier to apply to the land. Again, no great expense is justified in dealing with this material, but provisions, similar to those described for Chance mud, will serve to dispose of most of these lime wastes. In districts where fairly pure lime can be obtained at moderately low prices, it is difficult to cover the costs of handling these waste materials, since in no case are they sufficiently concentrated to allow two tons to do the work of one ton of high quality burnt lime. In districts where high quality burnt lime is only obtained with difficulty and at high cost, these industrial lime wastes are extremely important in agricultural practice, and every effort should be made to utilize them to the maximum extent.

There are hence three sources of waste lime from the alkali industry, one from the causticizing plant, one from the sulphur recovery plant and one from the magnesium carbonate works. The difficulty of dealing with these waste materials is due to their small agricultural value and the high cost of handling. The subject of the valuation of fertilizers is discussed on p. 188, where it will be at once seen that materials of this sort are difficult to deal in, on any practical business lines, at a price justified by their agricultural value. The steadily increasing costs of labour render it more and more difficult to utilize waste materials of low intrinsic value. On the other hand the increasing demands for food production will compel more complete utilization of all available materials.

Sulphuric Acid.—The manufacture of sulphuric acid is an important part of the alkali trade, but, as much sulphuric acid is made into superphosphate on the spot, the process is described on p. 128.

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Section V.—PLANT AND ANIMAL REFUSE OF VALUE AS MANURE

Guano.—The name "guano" is of Spanish origin, and was originally applied to the dried excrements and waste of sea birds. The accumulation of these residues, through many ages on the coast and islands in rainless districts, produced a material which is now known as guano. The original guanos were rich both in nitrogen and phosphates. The name "guano" is, however, also applied to deposits of similar origin which have accumulated in districts where there is much rain. In these rainy districts nitrogen constituents have undergone considerable decomposition, and have eventually been entirely washed out. There are several very different types of guanos, some containing much nitrogen, and others being chiefly phosphatic. The name guano is also sometimes extended to include various artificial products, such as fish guano and even blood guano, but these latter materials have little relationship to the original material to which the name guano is properly applied.

The earliest source of guano was from the islands of Peru. This guano was brought to Europe by Humboldt in 1804, but is believed to have been used locally from very early dates. The main deposits of Peruvian guano are now completely worked out. Guano was one of the most important early teachers of agricultural chemistry: it commanded very great confidence among practical farmers, because of its rapid action, and because there were no other manures on the market which supplied both phosphates and nitrogen in a readily available form. The old Peruvian guanos owed much of their effectiveness to the varied states of availability of their constituents. Some of the best qualities of Peruvian guano contained considerable quantities of rare nitrogen compounds; there has been recorded as much as

16 % of ammonium urate, 17 % of ammonium oxalate, 6 % of ammonium phosphate, and 11 % of ammonium magnesium phosphate. All these compounds are very uncommon, and are not found in any fertilizers other than guano. The phosphate present is partly there as potassium phosphate, but mostly exists as a calcium compound. Where the guano has been leached out by water, the percentage of nitrogen is very low. In some cases the percentage of calcium phosphate is also low, as well as the nitrogen, owing to the admixture of various quantities of sand and pebbles, and in some varieties this useless material may be present up to 20 %. Modern guano seldom contains more than 10 % of nitrogen; those qualities recently imported contain nitrogen 2–11 %, phosphates 15–40 %, and potash from 1 to 4 %. Some of the guanos now being excavated are of quite recent deposit, and contain feathers and other undecomposed material. The sea birds still inhabit their old haunts off the coasts of Peru and elsewhere, and are still depositing dung and waste substances for producing guano. Owing, however, to the smaller amount of decomposition, there is far less ammonium carbonate, and consequently less of the characteristic guano odour. In the case of phosphatic guanos, which have had most of their soluble material washed away, neither the nitrogen nor the phosphate have the same value as those materials in a high grade nitrogenous guano. The phosphate in these washed-out guanos is practically all tri-basic calcium phosphate, and is only superior to that of bones so far as it may be in a finer state of division.

The composition of all guanos is so variable that without an analysis of a given specimen no definite value can be attached to the sample in question.

When applied to the soil, the ammonia compounds of guano are rapidly fixed, and soon undergo the process of nitrification. Guano forms a very complete manure of a quick-acting character, and, being in a fine, dry powder, has the added advantage of easy distribution.

Bones.—One of the earliest of the phosphatic manures which was used in Great Britain was ordinary bones, which at

first were merely ground up and sold as ¼ in., ½ in., etc., bones. This method of employing fertilizers was a very crude one, as the fat in bones hinders their decomposition in the soil. The ordinary commerical bones supplied to bone factories contain 10 % of moisture, 10 % of fat, 18 % of nitrogenous matter, 44 % of phosphate of lime, 5 % of carbonate of lime, traces of phosphate of magnesia, soda, fluorine and chlorine. Where bones must be stored, it is desirable to sprinkle them with a little water containing carbolic acid or other convenient preservative. The chief sources of bones available for manurial purposes are the waste from kitchens, consisting of bones of the ox and sheep, together with horse bones from knackers' yards. In the condition in which bones are collected, they frequently contain 25 % of water. Horse bones are usually separated, because they produce a less valuable glue than the others. Bones of animals, which have been buried, have undergone some degree of decomposition, and have lost the whole of their flesh; these are dangerous things to deal with, as they may have come from animals which have died of infectious diseases and have been buried on that account. The bones, having been sorted, if necessary, and having arrived at the factory, are generally passed through a crusher or mill for the purpose of reducing them to a convenient size of about 1-in. pieces. It sometimes is necessary to use an electro-magnet to separate particles of iron from the bones. Should any sand, chalk, or earth be mixed with the bones in undesirable amounts, some kind of fine riddle will be necessary to separate this impurity from the bones. The crushed bones are placed in an extractor, which often consists of a vertical, cylindrical vessel, to which crude petroleum spirit, commonly called benzine, is added. The benzine is boiled by means of a closed steam coil placed in the bottom of the vessel. The benzine vapour carries away with it a considerable quantity of water contained in the bones. The benzine and water vapours pass away into a condenser, from which they flow in the liquid form into a separator tank. The separator tank possesses a glass gauge, which shows the dividing line

between the upper layer of benzine and the lower layer of water. By means of appropriately-placed taps, the benzine is run off into store, and the condensed water run to waste. When the bones have become sufficiently dried, the distillation of benzine is stopped by checking the circulation of steam through the steam coil. The benzine, which now contains the fat from the bones is run off from the bottom of the vessel, whence it flows to a still in which the benzine is distilled, condensed and returned to store. The grease left behind is then completely freed from benzine by blowing in steam; the resulting vapours are passed to the condenser and separator tank. Four or five washes with benzine in the extractor are generally needed. Other extractives than benzine, some of which are non-inflammable, are occasionally used; they are not very popular, owing to their cost. The grease can be used for soap making and other purposes.

In some works "degreasing" is conducted by older systems, in which the bones are merely boiled in open pans; in other factories the action of steam in closed vessels is employed. Under both of those systems, the manufacture of gelatine as well as the production of fat is generally carried out. For this double purpose, some factories slightly acidulate the water, in which the bones are boiled, by the addition of a very small quantity of sulphuric acid, say $\frac{3}{4}$ % of the weight of bones taken. The grease is set free from its calcareous compounds and 4–5 % of fat can thus be obtained from the bones. The steam process is carried out in large cast-iron cylinders, in which steam enters at the top and the fat runs off at the bottom; steam of from 2 to 4 atmospheres is generally used. As soon as the liquid contains a large proportion of gelatine, the solution becomes colloidal, the fat refuses to rise to the surface, so that the liquor appears milky. Care must be taken that the operation of boiling does not reach the stage of producing a colloidal solution. The operation must be stopped in time to allow the fat to separate by standing, after which the gelatinous solution is concentrated for the production of glue. The bones, having been freed from grease by any of these methods,

can then be ground up in a mill very much more finely than they could without preliminary treatment for the removal of fat. The manufacture of these materials into bone manures is described further on p. 173.

Wool Wastes.—Yorkshire mills produce a large amount of waste material which is known as "shoddy." Old woollen materials can be torn up in machines to produce fibre for re-making into cloth. During this process a large quantity of the wool becomes so cut up that it is unfit for spinning. There are also similar wastes from carpet, silk and other factories. Wool contains nitrogenous organic compounds which decompose in the soil with the ultimate production of nitrate, but cotton, having no nitrogen, produces no such result. Pure wool shoddy may contain as much as 15 % of nitrogen, and is much valued by the hop growers of Kent. By treating with sulphuric acid, wool can also be used as a valuable ingredient in admixture with other materials for fertilizing purposes. Shoddy is rather a slow-acting manure, but has given very beneficial results on many crops. Some of its value is due to its physical properties, such as its high capacity for absorbing water. It is usually ploughed in during the winter at the rate of 1–2 tons per acre.

Potash is an important by-product of the wool-combing industry. The method of washing raw wool that is usually adopted is to place it in hot water with alkali in very weak solution. By these means the fatty matter can be easily removed, but the liquors are more difficult to deal with. An important improvement consists in first washing the wool in cold water so that a small quantity of potassium carbonate is obtained in solution relatively free from fat. This practice was at one time very common because, owing to the high cost of soda, the potassium carbonate so obtained could be utilized for many purposes. The method has been revived recently owing to the shortage of potash. When the wool is first washed with water the solution is best evaporated to dryness and calcined, but the cost of evaporation and calcining is very considerable.

In the "Cardem" process the centrifugal wool-scouring

waste liquors are sprayed into an evaporator, and after concentration extracted with benzine. The extracted concentrated liquors are evaporated to a dry cake, which may contain 20 % potash, and can be used directly as a fertilizer.

Seaweed.—This old-fashioned source of soda and potash salts is once more coming into use. Japan claims to be able to produce potassium chloride from this source at a very cheap rate, under conditions which, if fully developed, would yield 7000 tons of potash salts per annum.

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SECTION VI.—THE UTILIZATION OF ATMOSPHERIC NITROGEN

FOR the purpose of obtaining nitrogen from the air in a form suitable for use by plants, almost all processes demand that some purification of the nitrogen in the air is necessary. Under modern conditions it is a common practice to obtain the necessary nitrogen by liquefying the air by one of the modern methods of converting gas into liquid by pressure and automatic cooling. These methods depend upon the following principles: (1) that if compressed air is allowed to expand without doing external work, there is a fall of temperature, due to the fact that internal work must be done in such expansion. With low temperatures and high pressures all gases can be liquefied. (2) That the boiling point of oxygen is 77·5° absolute, and that of nitrogen 91·5° absolute. (3) That by fractionation such liquids can be separated.

Air, compressed to about four atmospheres, is usually drawn through towers, and cooled by passing through a water tube to remove the heat caused by compressing the gas. It is then still further cooled by the waste gas proceeding from the rest of the process, by which means the moisture is condensed with the formation of ice, which is periodically removed. The air next passes through a cooler, which may be worked by ammonia, by which means the temperature is further reduced, and the gas purified from water and carbonic acid. Almost pure and dry air passes away from the fore cooler to the Linde nitrogen gas separator, where it is expanded through a valve and cooled down by an oppositely flowing current of nitrogen. The air then passes at a very low temperature through a coil, where it liquefies. The coils through which the gases flow surround a rectifier which works on the same principle as a distillation fractionating

column. The empty spaces are packed with wool and the outside of the machine is similarly protected. The liquid air is then led to a point near the top of the rectifying tower, down which it trickles, nitrogen coming off as gas and pure oxygen passing away from the bottom. Compressed oxygen is a valuable by-product of this process. Some moisture and carbon dioxide are usually condensed in the apparatus, which needs cleaning from time to time.

Nitrogen may also be separated from air by the Pictet process, according to which air, cooled down to liquefying point, is injected in the gaseous condition at a little over atmospheric pressure into a separating column over the plates of which liquid nitrogen is allowed to flow. This liquid nitrogen allows the air to be separated, as it permits the passage upwards of gaseous nitrogen, whilst gaseous oxygen is condensed by the cold produced by evaporating the liquid nitrogen. The mixture of liquid oxygen and nitrogen flows into the lower part of the fractionating column, where it continues to undergo fractionation in such a way that it reaches the reservoir at the bottom as liquid oxygen nearly free from nitrogen. In this process only one-fifth of the air to be separated is liquefied, nitrogen being kept in a gaseous condition during the separation; it is only a small fraction that is subsequently liquefied to maintain a sufficient flow of liquid nitrogen through the column. This subsequent liquefaction of a small proportion of the liquid nitrogen can be carried out by slight compression in closed coils placed on the oxygen reservoir and on the plates of the column, the pressure needed for liquefaction being obtained by a small compressing plant, so arranged that the pressures and temperatures are adjusted to condensing point according to the situation in the column. For example, a coil in the top of the column, where the temperature is $-196°$ C., requires only very slightly increased pressure to obtain liquefaction of the nitrogen contained therein, whilst a coil at the bottom must be supplied with a higher pressure. The heat evolved by liquefaction in the coils supplies the heat by means of which the mixture on the lower plates of the column is fractionated.

The system, therefore, of progressive choking is carried out through the entire ascending column of liquefying nitrogen.

By other methods air is passed over heated copper, oxygen being taken up by the copper and nitrogen passed on, the copper oxide formed being subsequently reduced by generator gas. Another method is to use producer gas, which consists of nitrogen, oxygen, carbon mon-oxide and carbon dioxide. The producer gas, mixed with a little air, is passed over a heated mixture of copper and copper oxide, when oxygen combines with the copper, forming copper oxide, and the carbon mon-oxide acts on the copper oxide, reducing it to metallic copper. The carbon dioxide so obtained can be absorbed either by lime or by a solution of sodium carbonate. When the latter process is used, pure carbon dioxide can be obtained as a by-product, after steaming the gas out of the sodium bi-carbonate formed. Another method of removing carbon dioxide is to compress the gas in the presence of water, when carbon dioxide dissolves. The water saturated with carbon dioxide is removed and the gas extracted by exhaustion, when the water can be used over again.

The subsequent utilization of nitrogen obtained in any of these ways will depend upon the particular process used. It may be converted into ammonia by the Haber process (p. 89), or it may be absorbed by calcium carbide and converted into calcium cyanamide (see p. 105). For the purpose of forming nitric acid by the arc process unaltered air can be used (see p. 97).

The fixation of nitrogen is also carried out in the field by the action of bacteria, either with or without the growth of plants to act as hosts. Experimental results have shown that among the bacteria which are most active, azotobacter is one of the most important. Such results can be observed by inoculating about 0·1 gramme of soil into 1000 c.c. of tap water containing 2 % of mannitol, 0·02 % of potassium phosphate, in the presence of calcium carbonate; the mixture is kept for some weeks at 27°–30° C. in a thin well-aerated layer in a conical flask. As an average of several results, about

9 milligrammes of nitrogen were fixed for each gramme of sugar decomposed. The nature of the carbo-hydrate presented to the organism is important. With xylose, a sugar obtained from straw, lactose and galactose obtained from milk, maltose and dextrin obtained from starch, and sucrose from cane or beet, the best results were obtained; other compounds also produced some fixation of nitrogen, but starch was rather inefficient. Much, however, depended upon the presence of calcium carbonate and other substances. The organism appears to have no power to utilize oxalic acid. Little is known of the chemistry of these changes and it is not known what becomes of the sugar. The only obvious product is carbon dioxide, fatty acids being formed only in small quantities. The nitrogen is found partly in compounds dissolved in the liquids, but mostly in the bacterial mass. It seems probable that the nitrogen is used chiefly by the bacteria for their own protoplasm. The organisms are extremely active, 1 gramme weight evolving 1·3 grammes of carbon dioxide in 24 hours. An adequate supply of phosphates is essential, any deficiency limiting the amount of fixation. Traces of nitrogen compounds are helpful in the early stages, but larger quantities reduce the amount of fixation, and may themselves suffer some change; for example, sodium nitrate is partially reduced to nitrite and ammonia. Algi can work in symbiosis with these organisms. In experiments extending over a considerable length of time, it was found that the fixation of nitrogen was much more rapid during the earlier stages than during the later stages. If the soil temperature falls as low as 7° C. nitrogen fixation ceases. Experiments in the laboratory and in the field show that azotobacter fixes nitrogen, provided it can obtain a sufficient amount of carbohydrate, and so long as the temperature is within certain limits. Where the soil is naturally deficient in some of the conditions necessary for nitrogen fixation, the application of appropriate fertilizers enables the azotobacter to carry out its function where otherwise it might fail to do so. The greater part of the nitrogen fixation in the soil is carried out by bacteria

acting in symbiosis with leguminosæ. These organisms enter the plant by first attacking the root hair, and a filament gradually extends up into the root, where the nodule begins to form; but beyond this the organisms do not penetrate. The organisms soon surround themselves with slime, and appear as bacterial rods. The organisms only enter, in any quantity, the particular species of plant to which they are accustomed, but they can be trained to attack other species, although they then lose the power of attacking their original hosts.

The process of the fixation of nitrogen by bacteria can be worked artificially. Leguminous plants can be made to grow perfectly without organisms by means of feeding with nitrogenous compounds. On the other hand, the organisms can be grown on artificial media containing carbohydrates, nitrogen being obtained from the air. The fixation of nitrogen soon ceases unless the resulting compounds are removed; Golding has attained this end by an ingenious filtering device, and has succeeded in fixing considerable quantities of nitrogen. Nitrogen fixation is known to take place in the nodule, which becomes richer in nitrogen than the rest of the plant, and it is assumed that the final product is a soluble protein which is passed on to the plant.

At Rothamsted experiments show that where no clover was grown barley produced 37 pounds of nitrogen per acre in the crop, but where clover was grown with the barley the amount of nitrogen in the crop was 151 pounds. The nitrogen left in the soil was 0·142 % where there was no clover, and 0·152 % where clover was grown. Similar results have been obtained at Cockle Park, where, by treatment with basic slag, land has steadily accumulated nitrogen. The plot which received no manure decreased in its nitrogen content from 0·197 to 0·174 % in seventeen years' time, but the plot that was treated with basic slag rose in nitrogen content from 0·227 to 0·244 % in eight years' time. With the presence of the basic slag, the organisms had been able to develop and fix nitrogen in the soil in considerable quantities, but without proper manuring they had been unable to keep pace with the inevitable losses by drainage.

Many attempts have been made to fix nitrogen commercially by the aid of bacteria without much practical success.

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PART III.—THE MANUFACTURE OF FERTILIZERS

SECTION I.—INORGANIC NITROGEN FERTILIZERS

THE nitrogen fertilizers differ from one another in chemical and physical properties to a remarkable extent. Such fertilizers as ammonium sulphate, sodium nitrate, calcium cyanamide and protein exhibit no physical resemblance to one another, and no chemical resemblance, excepting that they all contain between 15 % and 20 % of nitrogen. That such a varied assortment of materials should exhibit similar effects on plant growth is due to the fact that they all decompose in the soil with the production of calcium nitrate. Ammonium sulphate, $(NH_4)_2SO_4$, contains nitrogen in the form of an alkaline substance ammonia; sodium nitrate, $NaNO_3$, contains its nitrogen in the fully oxidized form of nitric acid: both these materials are nearly pure chemical compounds very stable and easily soluble in water. Calcium cyanamide, $CaCN_2$, is a very peculiar organic compound. In the crude form of the fertilizer as manufactured, only 50 % of pure calcium cyanamide occurs. Calcium cyanamide is not very stable, and dissolves very easily in water. Protein contains its nitrogen in the form of complex amino acids. As a rule, the protein is insoluble in water when it may be regarded as a colloidal "gel." When the protein is soluble it forms a colloidal solution. Protein forms an excellent food for most forms of soil organisms, and is broken down by them into simpler nitrogen compounds.

Sulphate of Ammonia.—The ammonia liquor obtained from gas works, coke ovens, blast furnaces, etc., as described on p. 48, is used for the manufacture of ammonium sulphate by a process of distillation. Other methods which

avoid distillation are completely out of date. Fig. 2 shows a typical plant for the preparation of ammonium sulphate from ammonia liquor. The liquor first enters

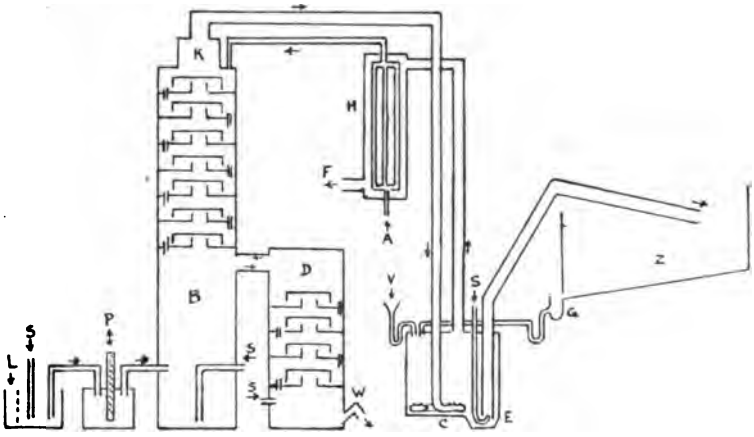

FIG. 2.—Sulphate of ammonia still.

L indicates the place where lime is added; by the side is a grid to prevent large particles of lime blocking the pipes.
S indicates several steam pipes which admit steam (1) into the lime tank to make milk of lime; (2) to the two stills to expel ammonia from solution; (3) to the ejector which blows the finished sulphate of ammonia from the saturator to the storage box.
P indicates the piston of the pump which forces the milk of lime into the lower portion of the still. The two valves which convert the oscillatory movement of the piston into a unidirectional flow of fluid are not shown in the diagram.
A indicates the point at which ammonia liquor enters.
H is the heater in which the waste heat from the saturator heats the ammonia liquor to near the boiling temperature. After being heated the ammonia liquor flows to the first still where steam drives out the ammonia gas. By flowing over a series of trays a gradual fractionation takes place.
B indicates the lower or lime portion of the main still.
D indicates the second still for distilling the "fixed ammonia." Between the two stills a wide pipe permits steam to pass one way and liquor in the opposite direction.
K is the head of the main still and prevents priming.
C is a lead coil from which the ammonia gas enters the saturator.
V is the point at which the vitriol is added. In practice a steady stream of acid can be maintained.
E is the ejector of the sulphate of ammonia.
Z is the store of finished sulphate of ammonia.
G is a gutter which returns the mother liquor to the saturator.
W is the exit for waste lime.

a heat interchanger, by which means the ammonia liquor is heated to somewhere near boiling point, but in small works

this preliminary heating may be omitted. The liquor then passes down through the still proper, which consists of about six or eight sections, each forming a small still in itself. Steam is passed up through these columns in the opposite direction to that in which the ammonia liquor flows down. By these means some of the ammonia compounds present in the liquor are broken up by the action of steam and heat. Ammonium hydrogen sulphide produces ammonia and hydrogen sulphide, both of which pass away: $NH_4HS \rightleftharpoons NH_3 + H_2S$. Ammonium hydrogen carbonate breaks up into ammonia, water and carbon dioxide: $NH_4HCO_3 \rightleftharpoons NH_3 + H_2O + CO_2$. Ammonium cyanide gives ammonia and prussic acid: $NH_4CN \rightleftharpoons NH_3 + HCN$. All these gases pass away out by the wide exit tube. A considerable amount of fractionation takes place in such a still, so that the ammonia coming out at the top is not admixed with an unreasonable proportion of steam. The ammonia liquor, having lost some of its constituents as described above, passes into a lower section, where it is mixed with lime. Milk of lime is prepared in a separate vessel by blowing in steam, the rough lumps of lime being usually separated by a perforated diaphragm from the rest of the tank: $CaO + H_2O = Ca(OH)_2$. A pump forces the lime and water into the lower part of the main still, where a steam pipe maintains agitation. In this part of the apparatus ammonium chloride and ammonium sulpho-cyanide and other non-volatile compounds of ammonia yield up their acid portion to the lime, so that the ammonia is set free,

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$$
$$2NH_4CNS + Ca(OH)_2 = 2NH_3 + Ca(CNS)_2 + 2H_2O$$

The limed liquors then pass out through a side tube into a smaller still, where distillation by steam is continued. By these means the ammonia is completely removed from the liquors, and waste lime passes out through the exit. This waste lime is sometimes retained, and can be used in place of the old-fashioned gas lime for application to the soil as a fertilizer. With correct working, little lime is

left unacted on, when the agricultural value of this by-product becomes small. The ammonia gas coming out of the main still now passes away through a wide pipe to the saturator, which is a lead-lined vessel. Sulphuric acid is admitted to the saturator in a slow, steady stream, at such a rate as to neutralize the ammonia coming in. Ammonium sulphate separates out, and is blown up by steam into the wide exit pipe, where crystals of ammonium sulphate and a strong solution of ammonium sulphate are forced out together in a soup-like condition into large wooden reservoirs, where the ammonium sulphate rapidly crystallizes, and the small amount of mother liquor drains away and is returned to the saturator. The gas coming out of the main still contains, as described above, hydrogen sulphide, carbon dioxide and hydrogen cyanide in addition to the ammonia. On passing through the sulphuric acid these added gases are not absorbed, but pass away through the exit. As the combination of ammonia and sulphuric acid gives rise to much heat, the gas passing away from the saturator is far above 100° C. and can be used to pre-heat the ammonia liquor. The gases passing away are then usually sent through an iron-oxide purifier box, smaller but similar to those employed in the purification of coal gas. When the iron oxide contains a sufficient amount of sulphur, it is burnt in the pyrites burners in a sulphuric acid plant, to recover the sulphur. A portion of these gases, containing hydrogen sulphide and carbon dioxide, with traces of prussic acid, is used to purify the sulphuric acid. Pyrites sulphuric acid always contains arsenic, which can be precipitated by hydrogen sulphide, even in the presence of strong sulphuric acid. The yellow arsenic sulphide is filtered off through special porous bricks or through a sand bed. At present no satisfactory use has been found for this arsenic sulphide. If arsenic had been left in the sulphuric acid, a yellow arsenic sulphide would have been precipitated in the saturator, and would have contaminated the ammonium sulphate. From the immediate point of view of the producer, discoloration reduces the market value, but, in addition, the presence of arsenic

would have been objectionable as a manure, since arsenic applied in manure to crops is liable to be taken up by the crops themselves. When arsenic is applied to the soil as an impurity in a manure, it passes into the barley grain, and thence into the beer brewed from malted barley. Although the amounts likely to pass in this way are undoubtedly small, the consumer naturally objects. The hydrogen cyanide may also be a cause of some slight difficulty owing to the colour which it produces in the ammonium sulphate. Should local alkalinity occur, ammonium cyanide would be formed, and as small amounts of iron are sure to be present, and would be reduced to the ferrous state by hydrogen sulphide, the conditions are suitable for the formation of ammonium ferro-cyanide : $6NH_4CN + Fe(OH)_2 = (NH_4)_4FeC_6N_6 + 2NH_4OH$. On the local alkalinity being replaced by acidity, ammonium ferro-cyanide and ferrous salts in solution will react, and, after exposure to air, produce Prussian blue, resulting in the formation of a blue ammonium sulphate. Hofmann, Arnoldi and Hiendlmaier found that when the reacting substances were equivalent to $FeSO_4 + 6HCN + 4NH_3$ the precipitate after oxidation had the formula $Fe_2C_6N_6NH_4,1\frac{1}{2}H_2O$, but when the proportions reacting were $FeSO_4 + 6HCN + 2NH_3$, $Fe_2C_6N_6H.2H_2O$ was formed after oxidation.

In the presence of air, local alkaline conditions would also produce ammonium cyanide which, acting on the free sulphur, produced from hydrogen sulphide by oxidation, would form ammonium sulpho-cyanide, NH_4SCN. Subsequently a ferric sulpho-cyanide, $Fe(SCN)_3$, which possesses a red colour will be formed, and under these conditions the ammonium sulphate will be coloured red. Both the blue and red colours are avoided by preventing local alkalinity. In some old forms of apparatus the gases passing into the saturator enter by a wide funnel-shaped pipe. This arrangement is liable to produce coloured products, as this system favours local alkalinity. It is now more common to use a coil of lead pipe, perforated with small holes, through which the ammonia gas is driven with some small amount of force,

thus maintaining more perfect agitation and so preventing local conditions of alkalinity. As iron always occurs in the sulphuric acid and is reduced to the ferrous condition by hydrogen sulphide, the ammonium sulphate will always contain crystals of ammonium ferrous sulphate, which slowly oxidize in air to red ferric compounds. Hence a very pure, white ammonium sulphate may be obtained in the first instance, which slowly changes to a pale yellow colour on exposure to air. This action is, however, usually only superficial, very slow and very slight. All the pipes in, approaching to and leaving the saturator must be lead, or at least lead-lined, but the latter portion of the exit pipe is often replaced by a wooden trough.

A good many variations occur in the details of construction in this apparatus. Floor space can be saved by constructing the main still on top of the secondary still. The saturator, as represented on p. 84, may be replaced by a half-open saturator, in which the ammonium sulphate is fished out by a perforated ladle, but in all cases the exit gases containing hydrogen sulphide must be removed, and either burnt or the sulphur recovered. The sulphate of ammonia may be separated from its mother liquor by a centrifugal separator.

The acid used, as a rule, is fairly strong—about 1·7 specific gravity—but in some methods slightly weaker acids are used. The resulting ammonium sulphate usually contains between 20 % and 21 % of nitrogen, or 24–25 % of ammonia, equivalent to from 93 to 99 % of pure ammonium sulphate. Generally it contains from between 0·1–0·5 % of free sulphuric acid, but special efforts are now being made to reduce the acidity to as low as 0·02 % with some considerable success. Some of the gas companies are producing a fine dry sulphate of ammonia which neither dries nor cakes and contains 21·1 % of nitrogen, no free acid and only 0·03 % of water. Owing to the fact that the saturator is at a higher temperature than the still, there is little tendency for any volatile organic matter to accumulate in the saturator, hence there is no trouble with discoloration by tarry

materials. Where the sulphuric acid is not previously purified, it is sometimes possible to skim the arsenic sulphide from saturators of an open type, but this is not a very satisfactory method of dealing with the difficulty. Some effort has also been made to convert the waste hydrogen sulphide into pure sulphur by the "Claus kiln" method. The result is not very satisfactory, as the sulphur is nearly always contaminated by some tarry materials.

In the ammonia plants attached to some of the large coke ovens, efforts are now being made to produce ammonium sulphate by the direct action of sulphuric acid on the gas, without the preliminary production of liquor. When this process is adopted, the gas is cooled by passage through a heat interchanger, to deposit tar and a small amount of ammonia liquor. The gas is then heated up again, by passage through the other side of the heat interchanger, and passed through sulphuric acid. Thus the ammonium sulphate is produced at a temperature considerably higher than that at which the gas has deposited its tar. The same risk of producing coloured salts occurs in this process as in the distillation method. As a certain amount of ammonia liquor is produced by this method, a small ammonia still is worked in the usual way, but the major part of the ammonia is absorbed directly.

Synthetic Ammonia.—In recent years attempts have been made to synthesize ammonia from nitrogen and hydrogen in the presence of a catalyst. (See Haber in References to this section.) At high temperatures appreciable quantities of ammonia can be made. Very great difficulties occur in this manufacture, owing to the engineering difficulties of working under very high pressures. The demand for ammonia is, however, a great one, and is likely to increase, owing to the necessity for the use of increasing quantities of sulphate of ammonia for fertilizers; it is highly probable that more use will be made of this method in the future. Up to the present it is known that no less than about one million tons synthetic ammonium sulphate has been manufactured in Germany, but the published information regarding

the process is extremely scanty. It has long been known, that on leading a mixture of nitrogen and hydrogen over certain catalysts, such as manganese, small traces of ammonia are produced, even at atmospheric pressure, but it is only at high pressures that commercially satisfactory results can be obtained. The first step in the industrial synthesis consists in the choice and adoption of appropriate means for manufacturing nitrogen and hydrogen in a fairly high degree of purity, above all free from catalyst poisons of any nature. Methods for producing mixtures of nitrogen and hydrogen from producer gas suffer from the fault that the last traces of carbon monoxide are difficult to remove. It is simpler and more satisfactory to prepare nitrogen directly from the air (see p. 77). The manufacture of hydrogen also presents some difficulties. Electrolytic hydrogen is of little use, owing to its high cost, but hydrogen can be manufactured from water gas by a continuous method, in which water gas and steam are passed together over a catalyst consisting usually of an active form of oxide of iron. By the interaction of carbon monoxide with steam, carbon monoxide is replaced by carbon dioxide and hydrogen, according to the equation :—

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The carbon dioxide thus produced is absorbed by compression on to water, hydrogen sulphide and other impurities being removed by the usual iron-oxide purifiers of the gasworks type. It is found in practice that considerable quantities of carbon monoxide are still left in the gas, which may be eliminated by treatment with calcium carbide, or by soda-lime when the gas is heated and compressed. An intermittent method consists in alternately passing steam over red-hot iron and reducing the oxide so formed by water gas. Owing to the instability of carbon monoxide at high temperatures, it is decomposed partly into carbon dioxide and carbon. The carbon produced is deposited on the iron catalyst, interfering with its action, and leaving carbon

behind to subsequently react with steam, with the formation of carbon monoxide, in accordance with the equation :—

$$C + H_2O = H_2 + CO$$

The intermittent method may be modified by utilizing gas which contains sufficient carbon dioxide to prevent the separation of the carbon according to the above equation. Hydrogen obtained in this way is almost completely free from carbon monoxide, and contains as its chief impurity a little nitrogen, which, for the purpose of manufacturing ammonia, is no disadvantage. To synthesize ammonia from the mixture of nitrogen and hydrogen it is necessary to compress it to the very high pressure of about 180 atmospheres. The catalysts which are available, apart from the rare metals of the platinum group, consist of uranium and iron. The mass of the catalyst is generally iron, which is increased in activity by traces of some other substances; for example, the iron potash catalyst is one frequently used. The gas then passes to a refrigerator, where the ammonia is almost solidified at a temperature of $-77°$ C. The gas then returns to the catalyst, which is maintained at a temperature of about 650° C. The economy of working depends very largely upon the efficiency of the heat and cold interchanges, which utilize the heat and cold employed in different parts of the cycle. In the economical efficiency of the process too great care cannot be paid to these temperature interchanges.

The construction of the ammonia retorts presents considerable difficulty, not only on account of the high pressure, but also on account of the temperature, which approaches that of red heat. Moreover, there is a rapid deterioration of the wall of the vessel under the influence of ammonia at high temperatures. It is better to design the plant so that the retort is completely surrounded by a nitrogen chamber at the same pressure as that to which the mixture of gases in the retort is subject, the whole being surrounded by a wall capable of resisting the pressure. Owing to the high pressure a burst occasionally takes place, which usually results in a clean split. The method of heating the retort

presents some difficulties. Electrical heating produces many complications, but the temperature can be maintained by injecting into the chamber a sufficiently small amount of air to produce the necessary heat by the combustion of some of the hydrogen. Sometimes combustion is not complete, and small amounts of oxygen begin to accumulate in the gases which are circulating, resulting in a great increase in the proportion of oxygen, which may suddenly cause an explosion. It is estimated that the cost of synthetic ammonia under normal conditions should not amount to more than £10 to £12 per ton. There is at present such a general tendency for prices to rise all round, that this is probably a much under-estimated figure.

Ammonia can also be made from calcium cyanamide by passing steam at high pressure over that material.

Ammonium sulphate can be made from ammonia and sulphur dioxide which are pumped into water at about 50° C. (112° F.) in the presence of a catalyst. Many substances act as catalysts, but sulphur is one of the most convenient. Under such circumstances reaction occurs as follows :—

$$6NH_4HSO_3 + 3(NH_4)_2SO_3 = 6(NH_4)_2SO_4 + 3S + 3H_2O$$

The sulphur separates out and if the solution be strong enough ammonium sulphate crystallizes out. Heat is given out during the reaction.

At present hardly any other ammonia salts have been used for fertilizing purposes, but ammonium nitrate (see p. 101) may before long come into more general use.

It is now well known that modern improvements in the fixation of nitrogen are likely to affect the sulphate of ammonia industry ; indeed both technical journals and daily press give articles as follows :—

" Germany has solved the problem of the fixation of nitrogen as a commercial undertaking on a gigantic scale. In future, from the point of agricultural fertilizers, she is independent of any blockade."

The above is the substance of a statement made by Dr.

Edward C. Worden, the explosives chemical expert of the United States Bureau of Aircraft Production, Washington, after his return to London from a tour of inspection of the chemical industry in Germany.

Such views are entitled to respect, not merely from the point of view of war, but from the commercial and industrial result of Germany's conversion from buyer to seller of substitutes for sulphate of ammonia.

"Speaking generally," said Dr. Worden, "the chemical industry of Germany is, and has been since the Armistice, just as prepared for peace operations as though war had never interfered with it. The technical staffs of the great concerns are at their maximum numbers. The skilled workers seem as numerous as ever. The greatest achievement of the Germans lies in their working of a process for the successful fixation of nitrogen on a great commercial scale. The headquarters of this new industry is the Haber plant of the Badische Anilin und Soda Fabrik at Oppau, near Ludwigshafen, on the Rhine, to which the German Government since the Armistice has lent nearly 200 million marks.

"Begun since the Armistice, built with reinforced concrete, this factory has now between 8000 and 9000 actively employed. When completed it will have a storage capacity of 350,000 tons of ammonia ready to be turned into ammonium salts and a daily capacity of 2800 tons, an amount sufficient, with potash and phosphates, to give an abundance of fertilizers for all German agricultural purposes.

"This building is only one of seven now in course of construction, and its one storage shed is equal in area to the whole of St. Pancras Railway Station. A few months ago the site was an ordinary marsh, but to-day the building contains such an intricate piece of plant as I have never before seen in all my experience. Up to the present about £150,000 has been expended upon it. The machinery is automatic throughout, the plant is practically duplicated in every part, there are four tracks between each set of buildings, and each building contains overhead automatic conveyances. The success of the method employed—without

going into any technical details—is due to the exceptional conservation of heat, the adoption of automatic calorimetric instruments throughout, and an extensive knowledge of critical temperatures and pressures in the most important stages."

Nitrate of Soda.—The mode of occurrence of nitrate of soda in Chili has been described on p. 23. The crude materials so obtained are treated with water, so as to remove the valuable sodium nitrate, and leave as much as possible of the other materials behind. For this purpose boiling tanks are usually erected on a hill slope, so that the liquors may fall by gravity. The caliche, or crude nitrate of soda, is first broken up in an ordinary crusher to pieces 2 ins. or 3 ins. in diameter. Crushing to fine powder is avoided as much as possible, because very fine material packs too closely in the tanks to permit a proper circulation of water. In some works rolls have been used instead of crushers, to avoid the difficulty of fine dust, which clogs the extracting tanks, and to avoid large lumps, which are not easily penetrated by water. At a higher level than the boiling tanks it is usually necessary to have several large reservoir tanks, one for pure water, one for the weak liquor from washing and one for mother liquor from which nitrate has already been crystallized. The usual kind of boiling tank is 32 ft. long by 9 ft. high, by from 6 to 8 ft. wide, with a perforated plate raised 9 or 12 ins. from the bottom, with steam coils, and with doors for discharging the exhausted material. Owing to the large size of the tanks and the effect of high temperature on the caliche, the pressure on the sides is very considerable, so that cross bars are needed for strengthening.

In practice one of the tanks which contains the exhausted material from a previous extraction has first to be emptied, which is very trying work, owing to heat and steam; after this refuse material has been removed, it frequently sets solid in the waste heaps. The charge of 60 or 70 tons of fresh caliche is then admitted, and the five or six tanks are worked in rotation, the water going into the tank which is nearly exhausted and finally entering the tank which

contains fresh caliche. In this last tank the fresh caliche is boiled for two or three hours, the temperature rising to 112° C. (234° F.). In all, the caliche receives four or five washes. The strong liquor from the fresh caliche then flows into settling tanks, where mud deposits, the deposition of which may be hastened by the addition of some precipitating agent. The liquor then flows into crystallizing tanks, which are about 15 ft. by 15 ft. by 2 ft. or 3 ft. deep, with the bottom somewhat sloping. The liquors are left to cool and crystallize for ten or fourteen days. The nitrate, after draining, contains from about 8 to 10 % of liquor. The crystals, with their adhering mother liquor, are left to dry in the air, whilst the mother liquor is returned to the cistern for further working up. By exposure to air the crystals dry until the moisture is reduced to 2–3 %, when they are broken up with wooden mallets.

The details of the process of heating and boiling caliche depend on the facts that sodium nitrate is much more soluble in hot water than in cold, and that sodium chloride is equally soluble in either. A considerable amount of heat is needed to bring the water up to boiling point. At first cold water dissolves a large quantity of common salt as well as other salts, but as more nitrate is added and goes into solution the common salt is precipitated. This fine salt coats the large pieces of caliche, and interferes with the leaching out of the nitrate. The resulting nitrate of soda has the composition shown in Table 11.

TABLE 11.

COMPOSITION OF NITRATE OF SODA.

	First quality.	Second quality.
Nitrate of soda	96·50	95·20
Sodium chloride	0·75	2·50
Sodium sulphate	0·45	0·60
Moisture	2·30	1·70

Several details need consideration before designing any improvement in the method. The size of the lumps of the

raw material have a very important influence, because the large lumps are difficult to leach out, and the smaller powder blocks up the tanks. During boiling, the insoluble mass packs closely in the tank and prevents free circulation; attempts have been made by forcing a current of liquid through the tank to overcome this difficulty. The amount of fine material which causes so much blocking up often amounts to 25 % of the whole material; occasionally the caliche is riddled, and the very fine material actually wasted to avoid this trouble. The larger the amount of insoluble matter, the greater becomes the difficulty in effecting a complete separation. Where the caliche is rich in nitrates, the loss due to imperfect washing and blocking up with deposits of salt may not be very serious, but, with raw material containing from 17 to 20 % of nitrate of soda improvements in manufacture are necessary.

At present in many of the works only about 40 % of the total nitrate of soda is extracted, and probably 50 % is a good round average figure. The nitrate left in the refuse amounts to about 30 %, and there is about 20 % of loss due to leaks which occur from the drainage liquors in various parts of the process. Many attempts have been made to improve the whole system of working. By means of vacuum filters the nitrate solutions are separated much more perfectly from the insoluble matter, and the remaining pulp can be ground up and further treated. In some of the larger works, all the coarse material is treated by the old system and all the fine material by the new system. Weaker liquors are also employed, together with evaporators, so that the efficiency has been raised from 50 to 64 %. Since the introduction of the newer methods of working, the estimate of the possible length of life of the Chili deposits has undergone a remarkable revision. With the old system of working it was only possible to utilize the richer materials, which would have been exhausted by 1930; the ability to utilize deposits which do not contain more than 10 % or 20 % of nitrate of soda, has raised the probable remaining duration of these deposits from a few years to several hundreds of years.

Competition with synthetic nitrates will prove the surest incentive to the utilization of weaker deposits. The amount of nitrate actually extracted to date, in comparison with what is still in Chili, is a very small fraction.

Nitrate of Lime.—Nitric acid can be produced directly from the air by the action of an electric arc or any other means of obtaining a high temperature. The first really successful method of working this process was the Birkeland and Eyde Arc Flame. In this type of furnace an electric arc is produced by an alternating two-phase current between water-cooled electrodes, which are placed between the poles of a powerful electro-magnet in such a way that the terminals of the electrodes are in the centre of the magnetic field. The electric flame, so produced, assumes the form of a disc, and the arc is drawn into a half disc at every half period of the alternating current. When the arc starts, the air is heated, the hot air acts as a conductor and is attracted to one of the poles of the magnet. Since the magnet poles are shaped around the path of the incoming air, the hot air assumes a disc shape. As the length of the electric arc increases, the resistance becomes greater, until it becomes so great that a new electric arc starts from the points of the electrode; the current then breaks, only to re-form in the opposite direction, and be attracted to the opposite magnetic pole. For the purpose of using this disc flame, it is enclosed in a special iron furnace lined with firebrick, which lasts very well, because the temperature of the walls does not rise above 800° C. (1500° F.) in normal working, in spite of the fact that the flame is over 3000° C. (5432° F.). Air is driven, by means of a blower, into the furnace, and thence successively through the tubes of a multi-tubular boiler, a cooler, and the oxidation tower, as described under the head of the Kilburn Scott process. The temperature of the arc flame may exceed 3000° C. (say 5400° F.), but the temperature of the escaping gases is only between 800° and 1000° C. (say 1500°–1800° F.).

The Schönherr arc flame differs essentially from that of the Birkeland, as in place of magnets and magnetic fields the

arc is produced inside an iron tube of comparatively small diameter. The air is given a rotary motion, so that the arc

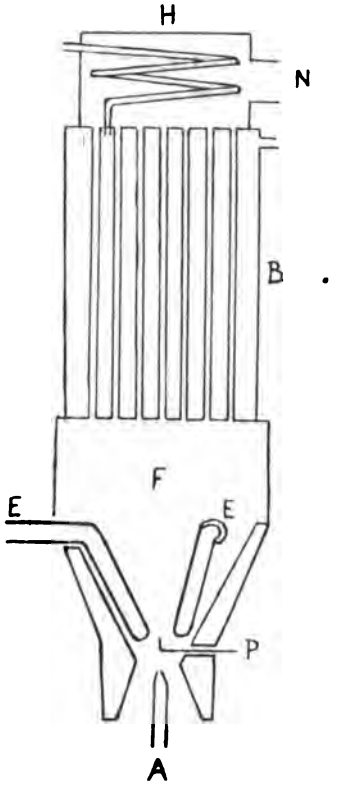

FIG. 3.—Nitric acid furnace. Scott-Pauling three-phase type.

A is the jet by which air is delivered into the furnace.
P is the wire conveying the pilot sparks which maintain the arc in action. The electric current is of very high tension from some kind of coil.
EE are two out of the three electrodes which supply the main current, and are so placed that the arc which is formed at their nearest points is in close proximity to the pilot sparks points, allowing the current of air to drive the arc up into the furnace.
F is the furnace, which is merely an empty space, allowing room for the flame to form.
B is the tubular steam boiler which generates steam from the hot flame of the nitrogen below. The hot gases then pass upwards from the boiler.
H is the pre-heater which heats the water supply for the boiler by the gases which have passed through the tubes of the boiler B.
N is the exit of nitrogen oxide, which passes away to the absorption apparatus.

burns almost as steadily as a candle flame. In this furnace the air takes an appreciable time to travel from one end of the furnace to the other, whereas in the Birkeland furnace the heating and cooling is much more rapid. The gases leaving the furnace contain about 2 % of nitric oxide.

The Pauling arc flame furnace possesses the special feature of a pair of water-cooled electrodes in the form of the letter " V," into the base of which a strong current of air is blown. The arc strikes at the lowest and closest portion, but the heat causes it to rise. This device has the effect of expanding the arc into the more spacious upper part of the " V," the flame so produced burning with great steadiness. The gases leave the furnace at about a temperature of 700°–800° C. (say 1300°–1500° F.). By working with a " three-phase " alternating current, Kilburn Scott has produced a furnace somewhat on the Pauling type, but owing to the " three-phase " system, supplemented by his device of " pilot sparks," it is possible to maintain a continuous arc. A special and separate high tension-current is produced for the purpose of maintaining a continuous passage of pilot sparks. The rapid removal of the products to regions of lower temperature is a great advantage, as it prevents the reversal of the formation of nitric oxide. In Fig. 3, p. 98, the furnace is at the bottom, and the flame plays directly on the bottom and tubes of the boiler, which serves the double purpose of cooling the gases and generating steam for general purposes in the works. Cooling the gases prevents the decomposition of nitric oxide to nitrogen and oxygen, and assists the oxidation of nitric oxide to nitrogen peroxide. The boiler is placed immediately above the furnace, so that the temperature of the gases is rapidly reduced. Further efficiency of the boiler is obtained by a superheater placed above, and the gases then pass away at temperatures not exceeding 200° C. (360° F.).

The resulting gases from any arc furnace, produced by the reaction $N_2 + O_2 = 2NO$, rarely contain more than 2 % of nitric oxide, and therefore require very bulky apparatus for subsequent treatment. The gases, leaving the furnace

at a temperature of 800°–1000° C. (1500°–1800° F.) are by all systems cooled as rapidly as possible by passing through boiler tubes to prevent decomposition due to reversion of the reaction. The temperature of the furnace gases is generally lowered to about 200°–250° C. (360°–480° F.). The second part of the reaction, where nitric oxide combines with oxygen, according to the equation $NO + O = NO_2$, does not take place at temperatures above 500° C. (980° F.), and only reaches a workable rate at temperatures below 200° C. (390° F.). To accelerate the oxidation of nitric oxide, the gases are conducted through a special cooling apparatus to lower the temperature. Part of this cooling may be carried out by passage through evaporators, where calcium nitrate is evaporated by this waste heat. In the end the waste gases pass through aluminium condensers, where the temperature drops to about 50° C. (122° F.). Owing to the slow rate of oxidation, the gas is then passed through some vertical iron cylinders with acid-proof lining, until the composition of the gases is about 98 % common air, and 2 % of a mixture of nitrogen peroxide and a little nitric oxide. The gases then pass away to the absorption towers, which usually consist of three series of stone towers about 60 ft. high and 18 ft. wide, down which water flows and absorbs the nitric acid. The remaining gases contain some nitric oxides, and pass through two wooden towers, filled with lumps of quartz, down which a solution of sodium carbonate is allowed to flow, producing sodium nitrite. The absorption follows the usual counter current-system, water flowing in an opposite direction to the flow of gas, so that the first tower contains the strongest acid and the third tower the weakest. The strength in the weakest tower is usually about 5 % of nitric acid, and that in the middle tower about 20% of nitric acid, while the strength in the strongest tower is about 40% of nitric acid. In the acid absorption towers the first action of nitrogen peroxide is to act upon water, with the production of nitrous and nitric acid, according to the equation: $NO_2 + H_2O = HNO_3 + HNO_2$. The nitrous acid

so produced subsequently breaks up, according to the equation: $3HNO_2 = HNO_3 + 2NO + H_2O$. In the wooden tower nitrogen peroxide and nitric oxide, when mixed together in the presence of water and sodium carbonate, behave as if they were nitrogen trioxide, that is, the anhydride of nitrous acid. The reactions are represented by the equation: $Na_2CO_3 + NO + NO_2 = 2NaNO_2 + CO_2$.

At present little attempt is made to produce free nitric acid from air for sale, but the dilute nitric acid obtained is treated in granite tanks with limestone, and the liquid evaporated, till it reaches a concentration equal to $Ca(NO_3)_2 . 2H_2O$. It is then run into iron drums, where it sets into a hard mass, in which form it can be exported, or it may be ground up into a coarse powder and filled into wooden casks. The material roughly corresponds to calcium nitrate, with two molecules of water of crystallization, and a common analysis is nitrogen 13 %, corresponding to anhydrous calcium nitrate 77 %, and 21 % of water, mostly as water of crystallization, and 1 or 2 % of insoluble matter, consisting of a little iron oxide and aluminium oxide, with some organic matter. In the wooden towers following the nitric acid towers, a mixture of nitrogen peroxide and nitric oxide reacts, producing sodium nitrite, which is used for commercial but not agricultural purposes. In all these methods a very large amount of electrical energy is expended for the production of oxides of nitrogen. Without cheap energy arc furnace methods are quite impracticable. Improvements are being made in details, so that one may look forward to a future decrease in the cost of this method of manufacture, if not absolutely, at least relatively to other sources of nitrates.

Ammonium Nitrate.—Whilst ammonium nitrate can be, and is, produced from nitric acid, made as described above, and ammonia, obtained from the distillation of coal, yet the high cost of the machinery needed for the direct oxidation of nitrogen is so great that other methods for the synthetic production of nitric acid have been developed. One of the most important of these is the oxidation of ammonia to

nitric acid, with the subsequent production of ammonium nitrate. For this purpose ammonia and air are passed together over heated platinum wire gauze. It is very essential that the mixture should be very well incorporated and move with a steady velocity, for which purpose the most satisfactory type of apparatus consists of an expanding cone followed by two or three perforated diaphragms, then a platinum wire gauze and lastly a reducing cone leading to the exit pipe. For the purpose of heating the platinum wire gauze an electric current is used. The oxidation of ammonia to nitric oxide gives rise to a considerable amount of heat, and this may suffice to maintain the platinum at the correct temperature.

In ordinary practice a pure, strong ammonia liquor, containing about 25 % of ammonia, is allowed to flow down a coke tower, up which air and a small amount of steam are allowed to pass. The mixture of air and ammonia needs to be filtered, to remove any particles of dust. Oxide of iron must be especially carefully removed, since it has a very harmful action upon the platinum catalyst. The platinum wire gauze is usually made from wire one four-hundredth part of an inch in diameter (0·06 mm.), woven into gauze with 80 meshes to the inch (32 per cm.), and mounted on an aluminium frame. Greater efficiency is obtained by using two or three gauzes close together. An output of about 1¼ tons of pure nitric acid per square foot of catalyst in 24 hours, with an efficiency of 95 %, has been regularly obtained. Without external sources of heat the efficiency drops to about 85 %. The hot gas which leaves the converter at about 400°–600° C. (750°–1100° F.), passes through a cooler, where its temperature is reduced to 30° C. (88° F.). The subsequent absorption of the oxides of nitrogen presents the same problem as does the arc method described above, but as the concentration of nitric oxide in the gas is very much greater, the size of the plant is correspondingly reduced. The gases obtained may easily contain about 10 % by volume of oxides of nitrogen. The dilute acid obtained may be neutralized by adding

ammonia. A particularly interesting use of this method of oxidizing ammonia to nitric acid is in conjunction with sulphuric acid leaden chamber systems, with which it is quite unnecessary to go further than to produce nitric oxide, which can be blown directly into the exit from the pyrites burners. For such a purpose quite a small plant is sufficient.

Pure ammonium nitrate contains 35 % of nitrogen, the samples commonly produced being about 96 % pure, and containing just over 33 % of nitrogen. It has an advantage over ammonium sulphate in that it contains nothing that is valueless for manurial purposes. Like many other very soluble materials, it often condenses much moisture from the air, but it does not differ very much from nitrate of lime in this respect. The deliquescence of ammonium nitrate, like that of any hygroscopic material, can be mitigated to some extent by dusting the crystals with any very fine dry non-deliquescent powder. (See p. 150.)

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Section II.—ORGANIC NITROGEN FERTILIZERS

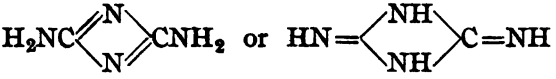
Calcium Cyanamide.—The first step in the manufacture of calcium cyanamide is to prepare calcium carbide, which usually forms a separate industry. Calcium carbide is made by heating lime and coke in an electric furnace. (See Witherspoon in References to this section.) The other material necessary for the manufacture of calcium cyanamide is pure nitrogen, the preparation of which has been described on p. 77. It is of the greatest importance for the manufacture of calcium cyanamide that the nitrogen should be pure. The presence of water in the nitrogen would decompose calcium carbide, with the production of calcium hydrate and acetylene, the presence of oxygen would produce calcium oxide and carbon, and either carbon monoxide or carbon dioxide would produce calcium oxide and carbon, according to the reactions :—

$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2$$
$$CaC_2+O \quad =CaO+2C$$
$$CaC_2+CO \quad =CaO+3C$$
$$2CaC_2+CO_2=2CaO+5C$$

The nitrogen is passed over the calcium carbide, which is heated in an electric furnace. The temperature at which calcium carbide is produced in an electric furnace, viz. about 3000° C. (5500° F.), is far too high. The calcium carbide after manufacture is cooled and ground, and then heated again in separate furnaces. The absorption of nitrogen takes place according to the reaction : $CaC_2+N_2 = CaCN_2 + C$. By adding calcium chloride, the reaction temperature for absorption of nitrogen is lowered to about 800° C. (1470° F.), whilst the addition of calcium fluoride permits absorption to take place at 900° C. (1650° F.).

About 2 % of either of these materials gives a good result. The nitrogen is generally delivered under pressure into the furnaces, which are heated to about 800° C. (1470° F.) by the passage of an electric current through a thin carbon pencil. The absorption of nitrogen is allowed to proceed for 30 or 40 hours, and saturation becomes apparent by a controlling gas meter. During the process the carbide is converted into a hard mass, not unlike coke. It is removed from the furnaces, ground either to a coarse grit or to a fine powder, and is then sold under the name of nitrolim. This substance usually contains from 50 to 60 % of true calcium cyanamide, with 20 % of lime, 28 % of silica and 14 % of carbon in the form of graphite. As calcium cyanamide picks up moisture from the air, its nitrogen content slowly decreases, so that by the time it arrives in the hands of the consumer the nitrogen varies from 18 to 20 %.

Calcium cyanamide generally contains traces of dicyanamide or dicyanodiamide. Cyanamide has either of the tautomeric forms $N : C . NH_2$ or $HN : C : NH$, the hydrogen being replaced by calcium. Cyanamide polymerizes to either



according to which form of cyanamide is concerned. The balance of evidence seems slightly in favour of the second formula. Cyanamide readily forms ammonia and nitric acid, dicyanodiamide forms ammonia, but poisons the nitrifying organisms, so that no nitrate is formed in the soil. Very little harm is observed in practice from traces of dicyanodiamide, but large percentages of the latter might be harmful.

Morrell, Burgen and Werner have shown that polymerization to dicyanodiamide is caused by small amounts of acids and alkalies, of which alkalies are the more potent. The process does not seem to be reversible. After application to the soil, cyanamide which contains dicyanodiamide does not produce its full amount of nitrate, but Rothamsted

investigations show that the plant can obtain its nitrogen in other forms such as ammonia or urea, both of which may come from cyanamide. Cyanamide containing dicyanodiamide should not be applied to a soil immediately before or after applications of sulphate of ammonia, as the nitrification of the latter will be checked.

Ammonium sulphate can be made from nitrolim by treatment with superheated steam, when all the nitrogen is given off in the form of ammonia, which can be condensed with sulphuric acid. Alternatively the ammonia so produced can be converted into ammonium nitrate, as described on p. 101.

Oil Cakes.—Some of the oil cakes, which are obtained as a by-product of pressing oil seeds, are not suitable for use as cattle food, but may be used for manure. When the resulting cake is only intended for use as manure, very crude and imperfect methods of pressing for oil are legitimate. The preparation of oils and fats from small oleaginous seeds, such as castor and rape, was originally performed by crushing the seeds and grinding them between stones, or grinding them in a large wooden pestle and mortar. Frequently some system of heating the meal was used, together with a certain amount of moistening. Presses which were driven home by means of wedges or screws were also used in primitive methods. On the larger scale, when the seed is received at the mill, there is first a preliminary operation of freeing the seeds from dust and sand, although this procedure is not of great consequence where the cake is only intended for manurial purposes. The seeds and nuts are sometimes decorticated, the shells being thrown aside and only the kernels being crushed and ground. The rollers used for crushing are generally finely grooved, although they are sometimes smooth. The material, after heating and moistening, is conveyed to the press, operated by a hydraulic ram, which presses the cakes upwards against a fixed roof. The meal is generally delivered, packed into closed measuring boxes, or into measuring boxes with cloths, open at two sides. In some systems the seed is

placed in a circular pressing cage, and the use of boxes is thus entirely dispensed with. Where the cake is intended to be exclusively used for fertilizing purposes, the method of extracting by solvents is frequently employed since a much greater quantity of oil is then obtained. As a rule, petroleum naphtha boiling below 120° C. (248° F.) is used. Carbon di-sulphide and di-chlorethylene can also be used for this purpose, but at the present time petroleum naphtha, frequently called benzine, is preferred. The chlorine derivatives are, however, advantageous, since they are not inflammable. These chlorine derivatives are not altogether advisable for the purpose of extracting cakes suitable for feeding, but for manurial purposes there is no objection to their use. Where solvents are employed, a coarser meal is used than where an oil press is worked. The temperature of extraction will make a considerable difference in the colour of the oil, and therefore cold extraction is often employed. Where the seeds and nuts are in a damp condition, it may be desirable to drive a little benzine vapour through to remove some of the water previous to extraction. The solution is then transferred to a steam-heated still, and the solvent driven off. The last remnants of volatile solvents in the oil are driven out by a current of steam. Sometimes a combination of processes is adopted, whereby a high quality oil is obtained by low temperature pressing, and the residual material is then extracted for the purpose of obtaining a second grade oil, leaving a cake suitable for fertilizers. Among the special cakes used almost exclusively for manurial purposes the following may be mentioned :—

Castor Cake.—Castor is pressed very largely in India for the purpose of making burning oil, which is much preferred locally to paraffin. Castor oil is also much used for lubricating purposes, especially for high-speed internal combustion engines. There are many different methods of pressing the oil from this seed. It has been crushed in a screw press, and the pulp put into boxes. About 37 % of cake and 27 % of husk is obtained by this simple process.

The seed is often roasted in a pot and pounded in a mortar with about four times its volume of water, which is kept boiling. The mixture is constantly stirred with a large wooden spoon and the oil skimmed off the surface. This process only gives a wet sludge instead of a cake, which, although it can be used locally as a manure, is of no use for export. The seed is sometimes soaked overnight in water, and then ground up with an ordinary pestle and mortar type of mill, the oil escaping through a hole in the mortar. The hole is easily choked by pieces of cake and needs constant cleaning with a stick. This method is generally considered to give the best fertilizing cake for local purposes. Considerable quantities are also sent from the local growing centres down to pressing mills in the large ports, where cakes similar to those produced in this country are obtained. Castor cake, having been obtained by any of these processes, is frequently milled and sold as castor meal. When finely divided it is much more suitable for application to the land.

TABLE 12.

	Castor cake, Bombay Presidency.			Castor cake, Bengal and North-Western Provinces.		
	Average (11).	Maximum.	Minimum.	Average (13).	Maximum.	Minimum.
Water	8·0	—	—	7·0	—	—
Organic matter	91·0	—	—	80·0	—	—
Nitrogen ..	3·75	4·2	3·1	6·9	8·0	6·1
Phosphoric acid	1·6	1·8	1·4	2·9	3·4	2·3
Potash	1·9	—	—	2·6	—	—
Lime	1·0	—	—	0·7	—	—

Rape Cake, Rape Dust and Rape Meal.—These manures are manufactured from brassica napus, the oil being expressed in crushers as for other oil seeds. Most of the rape seed comes from Russia, Germany, Austria-Hungary and India; in India there are two varieties grown, white and brown seed. Rape seed contains about 40 % of oil, and the manufactured cake frequently has 9 % left in it. Most of the rape cake manufactured is used for manure; although pure rape

cake can be fed in small quantities, it is liable to be contaminated with mustard, when it becomes very unsuitable for feeding. By breaking the resulting cake into dust, a much more suitable article for manurial purposes can be obtained. There is a popular idea that rape cake is useful for preventing the ravages of wire worm. It has been used at both Rothamsted and Woburn as a top dressing for wheat and barley, where it has proved a most effective material. Since the introduction of extractive methods of obtaining oil, a very large quantity of rape seed is now extracted with "benzine," and an extracted meal made from rape by this process is sold under the name of "Homco." The cake contains about 5 or 6 % of phosphates with 1 or 2 % of potash.

Fish Manure.—The sea has an inexhaustible supply of fertilizing materials. Apart from its own richness, it is constantly receiving organic matter from other sources. These materials all help to maintain the marvellous fertility of the sea. Possibly one of the reasons why the herrings have left the Baltic and approached the British Isles is the greatly increased population of the British Isles, and the large quantity of refuse which is consequently dumped into the sea. Various forms of vegetation in the sea are thereby encouraged in their development, providing an increasing supply of food for the fishes, which naturally congregate near the source of their chief food supply. During the herring season, when large numbers of fish are caught off the British coast, considerable quantities of fish refuse are obtainable; there are the heads and tails of the herrings which are cut off before salting; the herrings are generally split and gutted, and it is necessary to dispose of all these waste materials; there are, in addition, large numbers of worthless fish which are caught along with the useful ones. All these large amounts of material would become offensive in a very short time were they not converted into something harmless; the large firms controlling the fishing industry have been compelled, in their own interest, to establish large central depôts to deal with waste substances. A superior quality of refuse, obtainable from whitefish, is

generally only obtained in small quantities, and is for the most part converted into poultry food; the herring refuse and the special products obtained from livers are retained for fertilizing material. Under modern conditions of work, the materials are generally first cooked in jacketed vessels, with stirrers resembling paddles. At the same time, a strong draught of air is carried through these cookers by means of a fan. Thus, not merely is the odour, which is extremely objectionable, carried away, but the steam is carried away at the same time, consequently the fish refuse becomes dry. Winter whitefish needs practically no other process than cooking, and 30 cwts. of whitefish produce 6–7 cwts. of poultry food, but with other materials more elaborate systems of manufacture are carried out. When livers are available, these are boiled with steam and water, and the oil skimmed off the surface as far as possible; the remainder is then half-cooked, or partly dried by the steam paddle described above.

The semi-dried fish is then sent to an extracting plant, which most conveniently consists of a horizontal boiler enclosed and fitted with stirrers, so as to maintain the contents of the boiler in constant agitation; the boiler is "lagged" with the usual heat-preserving materials. A second plant preserves a partial vacuum, so that the temperature at which water is given off is lowered; at this stage of the process a further drying may take place if considered advisable. One of the great objects in heating at the early stages of the process is to coagulate the albuminoids, otherwise the material would be in such a colloidal condition that it would be difficult to obtain any separation between solid and solvent. Benzine, or crude petroleum naphtha, or the lighter fractions from the shale oil industry, are added at the rate of about 600 gallons to a 5-ton lot of dried fish refuse. The materials are slowly and steadily mixed up by the internal revolving paddle, and, should it be necessary that the contents be dried before proceeding any further, the space around the apparatus is heated with steam, and the vacuum somewhat increased, so that the benzine vapour

distils out, and carries with it much of the water vapour. By these means the water content can be lowered to the desired extent. After the material has become sufficiently dried and mixed up with benzine, the whole apparatus is allowed to rest: the benzine, which rises to the top, is run off by a side cock and pumped up to the steam-heated still, where the benzine is driven off, leaving behind the oil which has been extracted from the fish. The benzine is used over and over again. About three extractions are as much as it is practicable to give, and if 600 gallons of benzine are put into the boiler, about 400 gallons can be removed each time. Considerable quantities of benzine are left with the fish residue, but are distilled out with steam, which is admitted to the interior, and helps to drive out the benzine; as a vacuum is maintained all the time, very little steam need be admitted to the interior of the plant. Great ingenuity is exercised in reducing the loss of benzine, which has been so successfully conserved that only about $\frac{3}{4}$ % of the benzine is lost at each extraction. A 5-ton charge of half-cooked fish refuse yields about 25 cwts. of fish manure, but this varies somewhat with the seasons: June and July herring guts give 5 cwts. of fish manure from each 30 cwts. of refuse. The dried and extracted fish manure is removed by a door at the end of the cylindrical boiler, and at once put into sacks. Sometimes, after removal from the cylinder the material is ground, passed over an electro-magnetic roller to remove any fish hooks, nails and other iron objects which it might contain, and made to pass through a $\frac{1}{8}$-inch riddle.

The dust and fumes arising from this manufacture cause considerable difficulty and annoyance. The waste gases coming from the cooking plant are sent up flues and washed with water, the water running to waste. From the grinding mills where the dry material is ground up, a fan must be kept running to draw the fine fish meal away, which otherwise would cause a great annoyance to the workmen. The material is sucked away from the grinding mills in a very fine dusty condition, but can be separated by means

of a balloon, whereby the dust and air are blown into a large canvas bag, all the air having to pass through the canvas, and leaving the fine dust behind. (Fig. 4.) By tapping the bag, the accumulated dust can be shaken out at the bottom. This not merely removes the nuisance, but obtains some very valuable material, the dust being some of the richest fractions. The fish manure produced by these methods contains about 8 % of nitrogen, 6 % ot phosphoric acid and 1 % of potash. Other methods of utilizing the fish refuse have also been employed from time to time. According to other methods the fish is boiled, and the fish refuse pressed, this process closely resembling that of the seed oil process. Without boiling the fish it could be neither extracted nor pressed with any success. Boiling methods usually produce a different quality of material to that obtained by the extraction methods. Some varieties of fish contain far more phosphate and correspondingly less nitrogen than others. Refuse from the Newfoundland cod fishing contains about 5 % of nitrogen and 40 % of phosphates, owing to the large amount of bone contained in

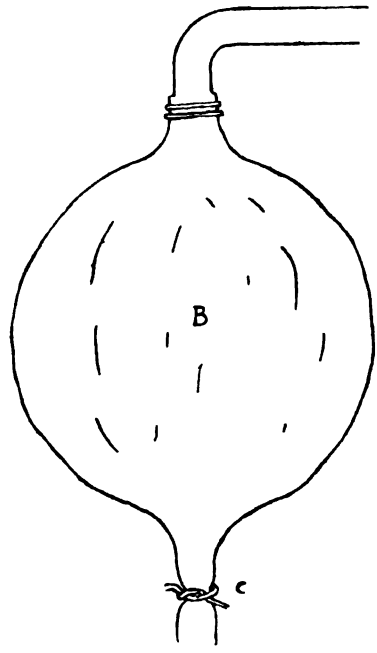


FIG. 4.—Dust-catching balloon.

A is the intake of dusty air blown by some fan.

B is the balloon into which all the dusty air is forced, and through the pores of which the air escapes, the dust being thus filtered out.

C is the exit pipe of the balloon, which is tied by a cord until the balloon has accumulated sufficient dust. The balloon is then beaten till the dust falls down into the exit tube (C), the cord is released, and the material is allowed to be blown into a sack.

the cod. In Brittany a similar article is produced by boiling the fish *débris* and pressing between iron plates, whereby an article containing about 6–7 % of nitrogen and 29–39 % of phosphates is obtained. Norwegian fish guano is chiefly obtained from cod, and is produced in a similar way to that of the British meal; it generally contains about 7–8 % of nitrogen and 12–15 % of phosphates. In the U.S.A. 9 % of nitrogen, 15 % of phosphates and 7 % of oil is the usual composition of fish guano obtained by a boiling and pressing process.

Blood Manures.—Fresh blood forms a red, thick liquid, which, in contact with air, soon separates into two parts—the solid fibrous part, which forms a clot, and the liquid part, which constitutes a serum. Of the total blood about 20 parts is solid matter, the remainder being water. The percentage of nitrogen in fresh blood is about 3 %, while the amounts of phosphoric acid and potash are almost negligible. Blood is generally dried by steam in an open pan, after the addition of a quantity of ferric sulphate solution, equal to about 1 part of solid, dry ferric sulphate per 100 parts of blood. The object in using ferric sulphate is to coagulate the colloids in the blood, which make it difficult, and even dangerous, to boil. All colloids froth readily, as may be noticed when boiling milk. The coagulated blood is usually allowed to drain, whereby a certain amount of liquid runs away. More expeditious and less offensive methods have been devised which use a rotary steam-heated drier, connected to a vacuum receiver. Blood which has been coagulated and dried very carefully and slowly below 100° C. may contain as much as 13–14 % of nitrogen, but the ordinary kinds of black blood manure contain usually only between 6 % and 10 %. Blood can also be dried very readily by lime. One hundred parts of blood are mixed with from 1 to 3 parts of quicklime, which converts the blood into a solid cake that can be dried in the air without any putrefaction. The resultant mixture falls down to a fine, inodorous powder. No special plant is required for this method, which possesses the additional

advantage that the resulting material contains a small quantity of lime, and is thereby improved as a fertilizer. The rate at which decomposition takes place in the soil is more rapid with lime-treated blood than with ferric sulphate coagulated blood.

Meat Meal.—Butchers' waste of all kinds is first cut up into pieces and boiled in vats. The material can be conveniently extracted with benzine for the recovery of fat, and a material which is of greater manurial value is thus produced. Much of the ordinary commercial meat meal is really a mixture of meat and bones, and is made during the process of the manufacture of extract of meat. A large amount of this material is put upon the market as Fray Bentos guano, which is manufactured in Uruguay in connection with the manufacture of extract of meat and pressed beef. It contains 6 % of nitrogen and 10–20 % of phosphates.

Hoofs, Horns, and Leather.—Hoofs and horns make a very useful form of fertilizer. When they are in their natural condition they decompose very slowly in the soil and have little value, but by treatment they can be converted into valuable manures. The hoofs of ruminants are nearly pure protein, and contain 13–14 % of nitrogen. Waste whalebone and the refuse from whale fisheries also come into this group. These materials are best either roasted or steamed. When horn is roasted without overheating it becomes drier, and as it cools it becomes brittle, and is thus easy to crush. Steaming may be done in a cylindrical vessel with a false bottom, which can be charged with the horn from a man-hole in the top. Steam is then blown through the bottom and allowed to escape through a safety valve. After treatment for about an hour, the steam is cut off, and the steamed horn removed from a man-hole at the bottom. The horn has thereby become brittle, and can be easily ground up. Various leather wastes are also utilized in the same way.

When hides are received at a tannery for the purpose of manufacturing leather, they are first washed and soaked

in water. The hides are then soaked in a vat with lime or sulphide of lime, for the purpose of removing hair. Owing to the deep position of the hair bulb in the hides, some

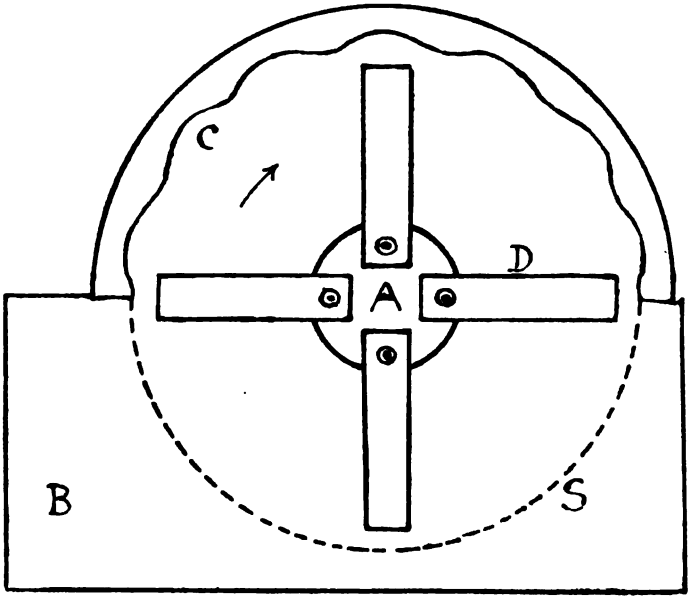


FIG. 5.—Disintegrator.

A is the axle on which the moving parts revolve; it is broadened out into a flat plate, to enable the arms to be satisfactorily attached.

D are the arms, which hammer the material to fragments. They are hinged on to the axle (A) so as to permit of movement should any unbreakable material be encountered. Normally, owing to the high speed, the arms are flung, by centrifugal force, into the position shown.

C is a corrugated roof, which helps in breaking the material flung against it by the rapidly moving arms. The speed of revolution is such that the peripheral velocity is about 3 miles per minute. Such a speed forces the air outwards and prevents a back blow through the feed intake.

S are the sieves, through which the material is forced by the current of air engendered by the centrifugal force produced in the air by the revolution of the arms.

B is the box in which the dust falls. Owing to the high velocity of the air currents induced, the box must be spacious to permit the deposition of the dust which, otherwise, would be carried away.

The corrugated casing (C) should have at least one section hinged, so that such an object as a horse-shoe, should it find access, could be easily ejected without cessation of work.

considerable degree of soaking is necessary before the hair can be removed. After softening the hair is scraped off with a knife. The lime and hair liquors produced in this

process are allowed to run away into ponds, where the water flows away and the solids settle out. After some air-drying a fertilizer is obtained which consists of lime compounds, with a fair amount of organic matter containing nitrogen. The composition of this material is very variable, wet samples containing ½ % of nitrogen and 13 % of lime, but if slightly dried the value may be easily doubled, or even trebled.

Various clippings of waste materials, known as fleshings, from the raw skins are sorted into two kinds, the dark coloured being used for joiners' glue and the pale for the manufacture of gelatine. They are well washed and treated with sulphuric acid, again well washed, and then boiled up in boilers for from 6 to 10 hours. A small amount of oil is skimmed off the top, the gelatine remains in solution, and the fibrous matter sinks to the bottom. This fibrous matter which is left at the bottom of the boiler is dried and sold as scutch. Being very fibrous, it must be broken up in a disintegrator, which produces a well-powdered material containing from 5 to 7 % of nitrogen. (Fig. 5.) Leather clippings, in the raw state, are of little value as a fertilizer, but by roasting or steaming some improvement can be effected. A better treatment is by means of acid. By using sulphuric acid of a specific gravity of about 1·6 %, heated to 140° F., raw leather and other organic nitrogen substances can be dissolved. The resulting mass then can be used for the manufacture of compound manures.

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Section III.—PHOSPHORUS FERTILIZERS

Phosphorus Compounds in Fertilizers.—The phosphorus compounds found in fertilizers do not exhibit the same variety of form as do the nitrogen compounds in the nitrogen fertilizers. Whereas nitrogen occurs in combination with hydrogen as ammonia, or with oxygen as nitric acid, or with carbon as cyanamide and organic nitrogen compounds, the phosphorus fertilizers are all substances containing some form of calcium phosphate. The varieties of calcium phosphate are, however, as numerous as the different forms of nitrogen in the nitrogen fertilizers.

Of the oxides of phosphorus only the pentoxide is present in fertilizers, and of the acids formed from phosphorus it is only pentavalent phosphorus that need be considered. The theoretical pentahydrate of phosphorus does not appear, but dehydrated forms thereof constitute the whole of the phosphorus compounds. Ortho-phosphoric acid, which may be represented as

$$H_3PO_4 \text{ or } PO(OH)_3 \text{ or } \tfrac{1}{2}(P_2O_5 \cdot 3H_2O)$$

is the most commonly occurring form in which phosphorus occurs. Pyrophosphoric acid, which may be represented by

$$H_4P_2O_7 \text{ or } P_2O_3(OH)_4 \text{ or } P_2O_5 \cdot 2H_2O$$

only occurs in substances which have been subjected to heat. Metaphosphoric acid, which may be represented as

$$HPO_3 \text{ or } PO_2 \cdot OH \text{ or } \tfrac{1}{2}(P_2O_5 \cdot H_2O)$$

is a product of overheating. The two latter forms, pyro and metaphosphoric acid, on boiling in acid solutions, are both converted into ortho-phosphoric acid. A similar change takes place in the presence of much water, even when the solutions are cold and neutral or alkaline, but the reaction

in this case is a very slow one. The calcium salts of ortho-phosphoric acid are present in all phosphorus fertilizers, and consist of :

(1) Mono-calcium phosphate or di-acid phosphate of lime, which may be represented by the formula :—

$$CaH_4(PO_4)_2 \text{ or } CaO \cdot 2H_2O \cdot P_2O_5$$

(2) Di-calcium phosphate, or mono-acid phosphate of lime, represented by the formula :—

$$Ca_2H_2(PO_4)_2 \text{ or } 2CaO \cdot H_2O \cdot P_2O_5$$

(3) Tri-calcium phosphate, or neutral phosphate of lime, represented by the formula :—

$$Ca_3P_2O_8 \text{ or } 3CaO \cdot P_2O_5$$

In addition to the above, there are crystalline forms of these substances, viz., the crystalline form of mono-calcium phosphate, represented by :—

$$CaH_4(PO_4)_2 \cdot H_2O$$

that of di-calcium phosphate, with the formula :—

$$Ca_2H_2(PO_4)_2 \cdot 4H_2O$$

which may also be represented by :—

$$CaHPO_4 \cdot 2H_2O$$

Tri-calcium phosphate is a doubtful substance, colloidal and jelly-like in appearance ; no convincing evidence is at hand to settle its exact constitution.

Another class of phosphorus compounds is represented by the apatite family. True apatite is a fluorine compound, having the formula :—

$$Ca_5(PO_4)_3F$$

which is a crystalline substance occurring in minerals and in the enamel of animals' teeth. The fluorine may be replaced by chlorine in the above formula, giving chloro-apatite. Most of the mineral sources of phosphates contain such materials. The fluorine in apatite may also be replaced by hydroxyl, giving a hydroxy-apatite, or the fluorine may be replaced by organic matter, giving an organo-apatite. In this last group may be included the chief constituent of bones,

where some of the phosphate occurs as a sclero-apatite, the gelatinous tissue of the bones taking the place of the fluorine. Some authorities consider bone phosphates to be a carbono-apatite $[Ca_5(PO_4)_3]_2CO_3$. There is also considerable evidence for supposing that the nitrogenous matter, insoluble in water, which occurs in milk, is a casein-apatite.

There are also special cases where calcium occurs as a basic phosphate, with more calcium in it than tri-basic phosphate, and where the acid concerned is less dehydrated than ortho-phosphoric acid. In addition, there are many complex silico phosphates, which are met with in some fertilizers.

In the presence of hydrochloric acid, mono-calcium phosphate is the stable form. If any of the calcium phosphates are dissolved in hydrochloric acid, and evaporated to dryness, it is mono-calcium phosphate that is left behind. Similarly, if a mixture of phosphoric acid and calcium chloride be evaporated, mono-calcium phosphate is left behind. Di-calcium phosphate will absorb hydrochloric acid gas passed over it. The weak acid carbonic acid can attack tri-calcium phosphate to a slight extent, and produce solutions which probably contain some di-calcium phosphate. The phosphates of the alkalies are all soluble in water. The phosphates of the alkaline earths are soluble in acetic acid, but insoluble in water; while ferric and aluminium phosphates are insoluble in acetic acid.

Basic Slag.—The occurrence of basic slag as a by-product in the manufacture of high-grade steel has been mentioned on p. 63. The crude slag is first obtained either as large blocks which have cooled slowly in the waggon into which the molten slag was originally run, or in large slabs obtained by pouring the molten slag on to a flat surface. Basic slag may be quenched in water for rapid cooling, but this process is somewhat dangerous, as the water may suddenly burst through a crack and boil explosively. Basic slag is a particularly difficult substance to grind in a satisfactory manner, as it is nearly always mixed with pieces of steel of varying sizes. These lumps of metal give much trouble in many forms of mill, but in mills which grind by

means of forged steel balls, the presence of a few other particles of steel does not make much difference.

The blocks of basic slag are usually first of all broken up by hand to eliminate the larger pieces of steel. A common stone breaker, consisting of two jaws meeting in a "V" shape, which move to and fro, is sometimes used for breaking up slag, but owing to the lumps of iron contained it is not very satisfactory. The resulting broken-up slag is then generally ground in a ball mill, in which a draught of air, caused by a fan or chimney, draws the fine powder away through sieves. The sieve used is a hundred-mesh sieve, containing 10,000 holes to the square inch, through which all the material should pass. In some cases coarser sieves are employed, so that only 80 % or 90 % of the finished product passes through the hundred-mesh sieve. The finished product may contain many small particles of iron, probably owing to some failure in the sieves of the ball mill. These particles of iron are extremely objectionable, as they block up the drill or distributor when the basic slag is applied to the field, and every effort should be made to reduce these metallic impurities as far as possible.

The ball mill used for grinding usually contains a large number of balls, which move round over steps, as in Fig. 7, p. 137. Basic slag, like most by-products, has a composition which has little relationship to the actual needs of the crop to which it may be applied as a fertilizer; there is yet a great deal of work to be done to discover all the points of value in basic slag. From time to time the method of manufacture is altered, so that empirical guides to the general nature of the composition of slag have no permanent value. When basic slags were first used, a test was devised by Wagner to extract the basic slag with a solution of ammonium citrate, but owing to the changes in manufacture this was subsequently altered to a test with citric acid. This method was originally designed to detect admixture with rock phosphate, but has been used to measure the solubility of basic slag for a long time. Collins and Hall showed that there was a distinct correlation between the citric solubility and the amount of

some of the constituents, and that the citric solubility increased with the lime content and decreased with the magnesia content. Robertson showed the arbitrary results of the citric solubility test (p. 126). Great difference of opinion has been expressed as to the value of the citric solubility indications; some find that they are of great value, and others find that they give results of little importance. As tested on the hay crop at Cockle Park, it was found that the slags of medium solubility were the most useful. When the results obtained from the hay crops at Cockle Park are put into curves, there is an optimum point in the curve, showing that the best results are obtained from slags of a medium composition. The extreme types of slag have not produced the best results. The only thoroughly reliable estimate of the value of the slag is its percentage of phosphoric acid. The fineness is undoubtedly an important point, both owing to the difficulties of distribution on the field, and on account of the different degree of solubility after application. Experiments to test this point were made many years ago at Cockle Park, in which it was found that slags approaching the standard of the 100-mesh sieve produced the best results, whilst those that were very coarse were almost useless. A few typical analyses are given in Table 13. In this table the citric soluble ingredients have been tested

TABLE 13.

ANALYSIS OF BASIC SLAG.

Total P_2O_5	per cent.	12·60	20·49	9·09	17·57	19·35
$Ca_3P_2O_8$	,,	27·50	44·92	19·82	38·34	42·24
SiO_2	,,	17·69	10·12	13·49	7·77	12·12
CaO	,,	38·02	46·81	40·43	52·22	44·75
MgO	,,	4·24	2·92	5·01	1·94	0·11
MnO	,,	7·39	4·38	5·41	9·37	4·68
Fe	,,	12·89	9·98	13·83	8·13	9·10
V	,,	0·48	0·66	0·23	0·38	0·30
Citric soluble P_2O_5 ..	,,	10·04	14·39	6·01	15·78	15·54
$Ca_3P_2O_8$ ..	,,	21·91	31·45	13·11	34·39	33·86
CaO ..	,,	32·50	31·68	28·69	40·14	32·96
Available lime	,,	20·63	14·62	21·59	21·53	14·64
Citric solubility ..	,,	80	70	66	90	80
Fineness	,,	85	88	95	77	82
Reducing power (FeO)	,,	13·63	7·31	13·24	8·10	10·70

according to Wagner's standard method of shaking up 5 grammes of slag with ½ litre of 2 % citric acid for half an hour, end over end, in a rotary shaker at a speed of about two revolutions per minute. When the citric soluble methods were almost universally adopted, it was found convenient to estimate the lime in the citric soluble extract, as one could safely assume that the citric soluble lime was of an active character. The available lime was calculated from the amount of lime soluble in citric acid, from which had been deducted the amount of lime combined with phosphoric acid in the citric soluble extract. Now that the determination of citric solubility is less frequently performed, the nearest comparable figure is obtained by taking the total lime and deducting the lime needed to combine with the total phosphoric acid. The figures would be somewhat higher than those given before, but would exhibit the same general relationship. In addition to the method of attempting to arrive at the available lime as expressed above, Hendrick devised a method of distillation with ammonium sulphate. Worked by his method, the amount of available lime is very near to that obtained by calculations from the citric soluble lime as given above. Usually his method gives 2–3 % higher. If the method suggested for the future of taking the total lime less the amount combined with the phosphoric acid is used, the figures obtained by such a calculation will be very close to those of Hendrick's method. One of the great advantages of basic slag over acid phosphatic manures lies in the fact that the former contains a considerable quantity of lime, which is capable of neutralizing strong acids like sulphuric acid in sulphate of ammonia, or feeble acids produced by organic matter in the soil. The products of bacterial growth in the soil also need lime or other bases. The lime in basic slag is probably present partly as phosphate and partly as silicate, yet this latter breaks up in the soil, so that the lime is undoubtedly useful. The true free lime, that is to say lime which is in the form of calcium oxide, is only present in slags to a very small extent, and has probably no significance.

The fineness is measured by the percentage which will pass a sieve containing 100 meshes to the inch. Occasionally the samples may show a degree of fineness much lower than the figures given above, but those lower than the lowest in the above table should be considered of doubtful value. The reducing power is determined by dissolving the slag in dilute sulphuric acid, and titrating with permanganate. This figure has often been alluded to as representing the ferrous oxide in the slag, but nothing is more certain than that this figure represents no such thing. It is given in the above table because it often appears in tables of analyses. Probably what is represented more than anything else is the amount of metallic iron present. If a slag contains ferric iron and metallic iron, the latter would reduce the ferric salts in solution to ferrous salts. In the equation $Fe_2(SO_4)_3 + Fe = 3FeSO_4$, it will be noticed that one part of metallic iron can reduce two parts of iron in the ferric condition, and return in the analysis three parts of ferrous iron. The opinion not infrequently given, that slags containing much ferrous iron are not easy to grind, is readily understood, when one remembers that it is mainly the quantity of metallic iron that is represented by the figures which state the percentage of ferrous iron.

Owing to the changes in the methods of manufacturing slag which have been introduced by using the basic open-hearth process, the composition of slag has undergone much change during recent years. Until comparatively recently, practically the whole of the phosphatic basic slag, which had been placed upon the market, contained phosphoric acid with a solubility of 70–95 % by Wagner's citric acid test. During the past few years, steel manufacturers, at least those using the basic open-hearth process, have been introducing fluorspar into the furnace, which has enabled greater quantities of lime to be added without making the slag too thick to flow conveniently. A special feature has been given to this new type of slag, since the fluorspar reduces the solubility of the phosphate in citric acid to only 20–50 %. Robertson has shown that although the first extraction with citric acid according to Wagner's method

gives only a small amount of phosphates, yet a second extraction will give a further considerable quantity of phosphate. Obviously, therefore, the citric acid test as designed by Wagner affords no reliable indication of the value of the slags, since the curve of solubility is cut at a purely arbitrary point, which seems to possess no particular meaning. Tables 14 and 15, which are copied from Robertson's paper, show the

TABLE 14.

DORMAN, LONG AND CO.'S BASIC SLAG.

Citric extract.	P_2O_5.	CaO.	Per cent. P_2O_5 of total.	Ratio P_2O_5.CaO.
	Per cent.	Per cent.	Per cent.	
1st	1·61	33·24	17·50	—
2nd	2·04	5·27	22·17	1 : 2·58
3rd	1·75	3·63	19·02	1 : 2·07
4th	1·34	2·66	14·56	1 : 2·00
5th	1·01	2·02	10·98	1 : 2·00
Extract totals ..	7·75	46·82	84·23	—
Actual totals	9·20	52·75	10·00	—

Total SiO_2 .. .. 17·10 per cent.

TABLE 15.

BELL BROS.' SLAG.

Citric extract.	P_2O_5.	CaO.	SiO_2.	Per cent. P_2O_5 of total.	Ratio P_2O_5 : CaO.	Ratio SiO_2 : P_2O_5.
	Per cent.	Per cent.	Per cent.			
1st ..	3·75	26·12	7·10	34·20	—	1 : 0·53
2nd	2·41	5·24	1·58	22·00	1 : 2·17	1 : 1·52
3rd	1·76	3·72	0·84	16·04	1 : 2·11	1 : 2·09
4th	1·10	2·35	—	10·00	1 : 2·13	—
5th	0·95	2·13	—	8·66	1 : 2·24	—
Extract totals	9·97	39·56	9·52	90·90	—	—
Actual totals	10·97	45·10	20·45	100·00	—	—

details of continuous extraction of slags with citric acid. It will be noticed that in one of these cases quoted above, there is more phosphoric acid dissolved in the second citric acid extraction than in the first. This is doubtless due to the fact that the first citric acid extract is weakened by the presence of much lime. In order to make quite sure that the fluorine was the real cause of this difficulty, Robertson took

2 grammes of a highly citric soluble basic slag and calcined it with fluorspar, and then submitted the resulting material to an extraction with 2 % citric acid. The results of subsequent analysis was that, in the first citric acid extraction, there was rather less than 30 % of soluble phosphates; in the second extract, 35 % more was obtained; and in the third extraction 24 % more, thus showing that fluorspar hinders the solution of slag in citric acid. It may be argued that the presence of fluorine hinders the solubility of phosphate in the soil as well as in the Wagner test, and this may reasonably be assumed until the contrary is proved.

A very large proportion of the basic slag which is now produced in Great Britain is of a low citric solubility. Many thousands of tons of fluorspar slag are produced annually as a waste product, and some firms even pay a few pence per ton to have this taken out to sea and sunk. It is a curious point to note that, in the United States, some of the rock phosphates which give a very low figure to Wagner's citric test are actually preferred to slags with a high citric solubility. By submitting slags and rock phosphates to continuous extraction, Robertson has shown that the rate of extraction by citric acid is more rapid in the case of the fluorspar slags than it is with the rock phosphates. The long discussions which have taken place on details about the solubility of basic slag now need revision as the result of altered conditions in manufacture.

Whatever the future may hold as to the relative importance of arable versus grazing farming, the amount of phosphatic manures that will be required for use in this country is certain to increase, and the supply of basic slag may be insufficient for application to grazing land and permanent hay. Under such conditions the only practical policy will be to use for grass land all the slags that can be ground economically and carried by rail and farm cart, and to make up the deficiency with the more expensive but quicker acting superphosphate or the cheap but slow rock phosphate. As basic slag is particularly suitable for grazing land on heavy clay soils, the right thing to do is to reserve the stocks of basic

slag for that land alone, and to use acid phosphatic manures for the remainder of the farm lands. There will remain to some degree a little choice between the use of finely ground rock phosphates and superphosphate, but it is not probable that undissolved rock phosphates can be used extensively, although there is much to be said for encouraging their use on certain particular classes of grazing land or permanent hay. Further, as shown on p. 187, there is much scope for mixtures of superphosphate and rock phosphate.

Superphosphate.—The attention of Lawes was drawn as early as 1837 to the problem of the better utilization of phosphatic manures. At that time machinery for grinding was far less efficient than it is now, so he fell back upon the use of a chemical means for improving distribution. It is quite possible, had he had at his disposal suitable ball mills, that the superphosphate industry might have waited many years before it became developed, but as things happened, the advantage of dissolving rock phosphates in sulphuric acid was very striking indeed. The new superphosphate so obtained was employed on a large scale on crops at Rothamsted in 1841, and in 1842 the results were so satisfactory that Lawes took out a patent for the manufacture of superphosphate. The treatment of bones with sulphuric acid had been practised before Lawes' patent, the novelty at the time consisting in the treatment of mineral phosphates. It is often forgotten, when alluding to the work of Lawes and Gilbert, that Lawes was a manufacturer of artificial manures quite as much as a farmer, and was probably as much financially interested in the business of manufacturing artificial manures as he was in the business of growing crops. When very finely ground, these mineral phosphates have much value, but by treatment with sulphuric acid their fertilizing efficiency can be enormously increased. The manufacture of superphosphate in Great Britain probably amounts to nearly a million tons per annum, and the total production of the world is about eleven times that quantity.

The first step in the production of superphosphate consists in the manufacture of sulphuric acid; although

the manufacture of sulphuric acid has other objects besides that of the production of superphosphate, nevertheless most of the sulphuric acid made in Great Britain is devoted to the manufacture of fertilizers, and only a small amount to other purposes. About 60 % of the total consumption of sulphuric acid is devoted to superphosphates and sulphate of ammonia. In the majority of superphosphate works, sulphuric acid is produced on the spot, and therefore the sulphuric acid industry is closely connected with the manufacture of artificial manures. As a result of this close connection, the production of sulphuric acid in Great Britain has followed directions which are especially suitable for the fertilizer trade. In the fertilizer trade, a weak and not a strong acid is required, and for this purpose leaden chambers are convenient.

The Manufacture of Sulphuric Acid for Fertilizers.—The first part of the process consists in burning pyrites in kilns. The lumps of pyrites are broken up into nuts, as free from dust as possible, and burnt in a long furnace. The heat of combustion of the pyrites is sufficient to keep the material alight, and no outside heat is necessary. Pyrites contains 40–50 % of sulphur, much iron, a little copper and some arsenic. The copper is left in the burnt pyrites, and is subsequently recovered at other works. The arsenic volatilizes and finds its way into the final product, sulphuric acid, where it remains as an impurity, unless subsequently removed (see p. 86). The waste iron oxide from gas purifiers can also be burnt in the same way. In recent years the use of zinc has increased. Zinc blende containing 30–40% of sulphur forms a difficult material for the manufacture of sulphuric acid, but as the manufacture of metallic zinc demands that first of all the ore should be deprived of its sulphur, sulphur dioxide is a waste product, and must be used somehow. The operation of burning zinc sulphide requires additional heat, usually supplied by the combustion of fuel which adds carbon dioxide to the gases passing into the leaden chambers. Carbon dioxide retards the chemical changes taking place in the leaden chambers.

A charge of pyrites in the burners usually lasts for about 24 hours, and the kilns are charged in regular succession, while the quantity of air entering the kiln is carefully regulated by a well-fitting door. Certain furnaces, of a mechanical type, have also been designed to deal with powdered pyrites. The fumes passing away consist of sulphur dioxide, nitrogen and oxygen, which are then drawn by a powerful draught through nitre pots containing a mixture of sodium nitrate and sulphuric acid heated by the gases proceeding from the pyrites furnace. The necessary draught is obtained by a tall chimney, sometimes assisted by a fan. The gases then pass up the Glover tower and meet a stream of weak acid from the leaden chambers mixed with the strong acid running out of the Gay Lussac tower, which delivers a strong acid impregnated with nitric oxide recovered from the waste gases passing away out of the leaden chambers. In the Glover tower interaction takes place between sulphur dioxide and nitrogen oxides, with the production of a certain amount of sulphuric acid and the evolution of nitric oxide. At the same time the heat from the pyrites burners evaporates water, in consequence of which the Glover tower is a means of concentrating the sulphuric acid produced. The acid running out of the Glover tower has been deprived of all its oxides of nitrogen and much of its water so that it can be used directly for the manufacture of superphosphate without any further concentration. The gases then pass away from the Glover tower through four or five leaden chambers, in which the oxidation of the sulphur dioxide is completed. The common explanation of the changes is given in the following equations :—

(1) $2SO_2 + 3NO_2 + H_2O = NO + 2HO.SO_2.NO_2$

(2) $2NO + O_2 = 2NO_2$

(3) $4HO.SO_2.NO_2 + 2H_2O + O_2 = 4HO.SO_2.OH + 4NO_2$

or

(1) $NO + NO_2 \rightleftarrows N_2O_3$

(2) $2SO_2 + N_2O_3 + O_2 + H_2O = 2HO.SO_2.NO_2$

(3) $2HO.SO_2.NO_2 + H_2O = 2HO.SO_2.OH + N_2O_3$

Steam is blown into the leaden chambers, so as to supply the

TABLE 16.

ESTIMATE OF THE QUANTITIES OF SUPERPHOSPHATE AND BASIC SLAG APPLIED TO THE CROPS GROWN IN THE UNITED KINGDOM BEFORE THE WAR.

Crops.	Approximate area.	Percentage manured.	Superphosphate.			Basic slag.		
			Percentage manured.	Dressing per acre.	Approximate quantity required.	Percentage manured.	Dressing per acre.	Approximate quantity required.
	Thousand acres.	Per cent.	Per cent.	Cwts.	Thousand tons.	Per cent.	Cwts.	Thousand tons.
Wheat	1,906	20	15	3	43	5	3	14
Barley	1,873	25	25	2½	59	—	—	—
Oats	3,899	20	20	2½	97	—	—	—
Beans	301	30	20	3	9	10	3	5
Peas	170	40	40	3	10	—	—	—
Potatoes	1,209	60	60	3	109	—	—	—
Swedes and turnips	1,761	60	50	3½	154	10	3½	31
Mangolds	517	65	50	3½	45	15	3½	14
Cabbage, rape, etc.	192	55	40	3½	13	15	3½	5
Vetches	138	20	10	2½	2	10	3	2
Other crops	400	20	20	2	8	10	2	4
Fallow	349	—	—	—	—	—	—	—
Rotation grass (hay)	2,903	25	20	2½	73	5	2½	18
Rotation grass (pasture) ..	3,703	5	3	2½	14	2	2½	9
Permanent grass (hay) ..	6,490	18	10	2½	81	8	3	78
,, (pasture) ..	20,860	3	1	2½	26	2	4	83
Total	46,671	—	—	—	743	—	—	263

TABLE 17.

ESTIMATE OF THE QUANTITIES OF SUPERPHOSPHATE AND BASIC SLAG REQUIRED TO SUPPLY MODERATE DRESSINGS OF MANURE TO THE CROPS GROWN IN THE UNITED KINGDOM, IF 3,600,000 ACRES OF ARABLE LAND WERE ADDED TO THE EXISTING AREA OF 19,400,000 ACRES.

Crops.	Approximate area.	Percentage manured.	Superphosphate.			Basic slag.		
			Percentage manured.	Dressing per acre.	Approximate quantity required.	Percentage manured.	Dressing per acre.	Approximate quantity required.
	Thousand acres.	Per cent.	Per cent.	Cwts.	Thousand tons.	Per cent.	Cwts.	Thousand tons.
Wheat	3,500	30	15	3	79	15	3	79
Barley	2,800	30	30	2½	105	—	—	—
Oats	5,000	30	25	2½	156	5	3	37
Beans	350	50	20	3	10	30	3	16
Peas	250	50	50	3	19	—	—	—
Potatoes	1,400	75	70	3	147	5	3	10
Swedes and turnips	2,000	80	70	4	280	10	3½	35
Mangolds	600	80	60	3½	63	20	3½	21
Cabbage, rape, etc.	190	60	40	3½	13	20	3½	7
Vetches	150	30	20	2½	4	10	3	2
Other crops	400	40	30	2	12	10	2	4
Fallow	360	—	—	—	—	—	—	—
Rotation grass (hay)	3,000	60	40	2½	150	20	2½	75
,, (pasture) ..	3,000	10	5	2½	19	5	2½	19
Permanent grass (hay) ..	6,500	50	25	2½	203	25	3	244
,, (pasture) ..	17,171	15	5	2½	107	10	4	343
Total	46,671	—	—	—	1,367	—	—	892

necessary amount of water. If the acid were allowed to become too strong, other reactions would take place, and certain amounts of nitrous oxide might be evolved. As a rule, the temperatures in most works in Great Britain are not sufficiently high to permit the use of water sprays in place of steam, but in countries where temperatures are higher, the use of steam only is found to give too high a temperature. Generally, the acid produced in the last of the leaden chambers is small in amount and weak in strength, and is of no use for the direct manufacture of artificial manures. It is very common to find that the works where superphosphate is made have some small side manufacture where this weak acid can be utilized. Where this is not the case, the weak acid must be concentrated. After leaving the leaden chambers, the gases then pass up through the Gay Lussac tower, down which strong sulphuric acid trickles. This acid is cold, and has a specific gravity of about 1·75. Partly owing to its high strength, and partly owing to its low temperature, nitric oxide is absorbed by the sulphuric acid. The nitrified acid so obtained is sent away to the Glover tower, where, owing to the dilution by chamber acid and the high temperature of the gases produced from the pyrites burners, nitric oxide is again given up. Owing to its low temperature, the Gay Lussac tower may be safely filled with coke, but the Glover tower is generally packed with acid-resisting bricks. The temperature of the gas entering the Glover tower is about 300°–400° C. (570°–750° F.), but when entering the leaden chambers it is reduced to about 50°–80° C. (120°–180° F.). The acid leaving the Glover tower has usually a specific gravity of 1·53 to 1·62. In the Glover tower the gravity of the acid may be raised to 1·7, with 79 % of pure acid; a higher strength cannot be obtained, as it would then begin to absorb nitrogen oxides. For fertilizer purposes it is not desirable to produce strong acids, and a gravity of 1·6 is usually aimed at.

" Reinforced lead " is made by coating iron wire with lead and embedding it in sheet lead. " Reinforced lead "

made into sheets and pipes withstands much higher pressure than pure lead of the same weight or thickness. This new material is sometimes used in the construction of leaden chambers and connections.

The annual production of sulphuric acid in the British Isles before the war was 1,000,000 tons per annum, reckoning the acid at 100 %, which is equal to about 1,500,000 tons of chamber acid. In 1918 just under a million tons of chamber acid and 300,000 tons of fuming acid were made in the United Kingdom, both amounts being reckoned at 100 % H_2SO_4. Since more than 60 % of the nation's acid production is used for fertilizer purposes, the sulphuric acid plants of Great Britain are almost always of the leaden chamber type. Acid plants were often thrown out of action for a time before the war, but during the war period the maximum output was aimed at.

For some years before the war the manufacture of superphosphate in this country was unsettled, and there was a gradual decline in the export trade, the maximum having been reached in 1911. The cause of this decline may be chiefly found in the erection of superphosphate plants in countries which have previously imported this material. It must not be forgotten that the British Isles possess no special advantages for the manufacture of superphosphate, since both pyrites and phosphate rock have to be imported as raw materials. It was chiefly due to the fact that most superphosphate works were associated with acid plant that the producers in this country were able to compete with foreign manufacturers. Some of the smaller works found great difficulty in keeping up to date, especially those having to purchase their acid from outside. Owing to the substitution of sulphate of ammonia for nitrate of soda in the British Isles, largely increasing quantities of sulphuric acid have been used in the production of ammonium sulphate. The production of ammonia is likely to increase in this country, and there may be a considerable increase in the demand for sulphuric acid in this direction. On the outbreak of war there was a lack of sulphuric acid, but, since the cessation of

the large demand for sulphuric acid in the manufacture of explosives, the supply has become plentiful, and now the problem is to use it all. In 1915 it was suggested that nitre cake or acid sodium sulphate could replace sulphuric acid in the manufacture of superphosphate and also partly replace that used for absorbing ammonia in the production of sulphate of ammonia.

During the war arrangements have been made in this country to bring over Australian zinc ores, which had formerly gone to continental works where they were converted into metal and sulphuric acid. The utilization of such sulphuric acid in this country will depend largely upon the development of the superphosphate industry. Opinions given by Sir Thomas Middleton and Sir Charles Fielding are in agreement as to the use of superphosphate becoming increasingly necessary in the future. As is natural in the case of such attempts to read the future, the figures are somewhat wide apart, but the lesson is the same. The available supply of basic slag shows little likelihood of reaching the amount required, and the manufacture of superphosphate or other phosphatic fertilizers must be increased accordingly. The extension of the export trade is a difficult problem, but perhaps Australia, South Africa and India will require quantities of phosphatic fertilizers, although they will doubtless make some of the necessary superphosphate. In Great Britain the future development of the fertilizer trade may be closely connected with the establishment of the zinc industry upon a sound economic basis. For the latter purpose it is essential that the works be situated in the neighbourhood of deep-water ports. Zinc sulphide is ill adapted to compete with pyrites as a source of sulphuric acid, but as sulphur dioxide must be produced in making zinc, it is only a question of bookkeeping to decide which item should be credited with the profit. The Avonmouth zinc sulphur plant alone was estimated to produce 200,000 tons of superphosphate per annum, and, should these works ultimately succeed and be extended, the position of the superphosphate industry would be very vitally affected.

Should any new uses for sulphuric acid arise, the situation might be improved. Among possible new agricultural uses may be named the destruction of weeds.

Dr. Winifred Brenchley reports :—" SULPHURIC ACID.—This is the most potent substance utilized for weed destruction, and owing to its corrosive nature needs very special precautions in handling. If properly dealt with, however, it proves effective in cases in which the more usual sprays are of little value. Sulphuric acid is one of the few sprays that has been found to clear grass land of bracken. A 5% solution causes the leaves to wilt within a few hours, and some days later the stems turn black and wither, because the acid is gradually conducted along the midrib and down the stalk, eventually reaching almost to the underground rhizomes. A new growth springs up later, but a second spraying disposes of this for the year and also weakens the plant for the future. Where the growth of bracken is dense the canopy formed by the bracken leaves protects the underlying herbage from the harmful effect of the acid, and as the following year the fern is later in appearing the grasses are able to get ahead earlier, resulting in an improved pasture.

" On the Continent, sulphuric acid is considered a safe spray for cereals if used when the crop has only about five or six leaves. It is much used in parts of France (Lot-et-Garonne) for destroying wild radish among wheat, 90–100 galls. per acre of an 8 or 10 % solution being employed. It is somewhat selective in its action, as certain weeds escape, especially wild oat (*Avena fatua*), medicks (*Medicago sp.*) and members of the lily family (as wild onion). It is, however, deadly to most annual and biennial weeds as poppies, charlock, corn buttercup, cornflower, wild carrot, radish, vetches and vetchlings, and it is said to be very effective in clearing these pests from badly infested fields. For general use 60–70 galls. per acre of a 10 solution is sufficient for oats, rather less being used for barley."

Grinding Rock Phosphates.—The other raw materials besides sulphuric acid that are used for the manufacture of superphosphates are some of the various rock phosphates,

which have already been described on p. 27. It is necessary that the raw phosphates should be very carefully ground, as the degree of fineness to which the phosphates are reduced contributes very largely to the success of the superphosphates. The phosphates are ground in different patterns of mills, according to the nature of the phosphates utilized. Some of the phosphates, on exposure to air, weather down to a certain extent, and when this is the case it is advisable to allow them to powder themselves, but in any case a considerable amount of grinding is necessary,

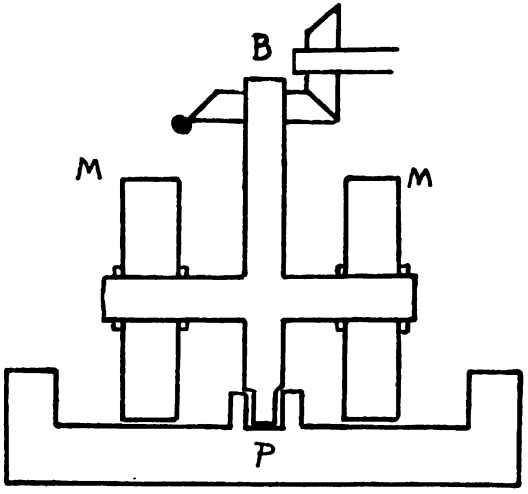

FIG. 6.—Section of edge runner.

B is the bevel gearing which transmits power to the runner.
MM are the two stone mill wheels which revolve.
P is the bed plate on which the grinding takes place. The rotation of the bevel gearing (B) causes (MM) to revolve, and as these rest upon the bed plate they execute a rolling and sliding movement, thus grinding the material to powder.

and the best mill to use will depend upon the kind of phosphates to be ground. A vertical edge runner (see Fig. 6), is still in occasional use, and permits of the disintegration of a great variety of substances. The ordinary flat stone mill and roller mill are also used, but the common modern grinding machine is the ball mill. The early forms of ball mill

are shown in Fig. 7, where a rotary drum is enclosed in a double envelope supplied with sieves. The balls, the number of which is variable, run on trituration plates forming segments of several chords to the circle of the sieves, so that by dropping off the edges, the balls hammer the material to pieces by shock, as well as grind it to powder by rolling. The substances ground in the ball mills pass through holes in the trituration plates, and fall on to a coarse sieve, and then meet the finer sieves. There is always some considerable wear and tear of the balls, depending on the nature of the phosphates and the kind of balls employed; forged steel balls last much longer than cast-iron balls. What may be described as a compromise between a ball mill and an edge runner is also employed in some factories, where a flat stone with deep grooves rotates on a vertical axis, and four heavy balls, of about 1 cwt. each, roll round in these grooves, the mill being completed with a cover and a series of sieves in a similar way to the common ball mill. The phosphates should be made to pass through a 60-mesh sieve, when a large fraction of the material is considerably finer than that. In practice 95 % of the final powder passes a sieve with 80 meshes to the inch, and 85 % goes through a sieve with 100 meshes to the

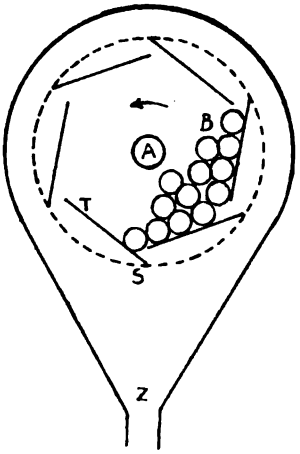

FIG. 7.—Section of ball mill elevator.

A shows the axle on which the moving parts rotate, in the direction shown by the arrowhead.

B are the steel balls which pound the material by falling by their own weight on to it.

T are the trituration plates, on to which the balls fall; the trituration plates of necessity are made of strong material firmly fixed. The trituration plates are set in steps, so that the balls must fall off one trituration plate on to the next.

S are the sieves, usually two in number, an inner cylinder of coarse material and an outer cylinder of fine material. The dusty material passes through these sieves into the outer space.

Z is the spout from which the fine powdered material is delivered.

inch. It may sometimes be found necessary with certain rock phosphates in coarse lumps, *e.g.* Algerian phosphates, to put them first of all through a Blake crusher. Where old-fashioned mills, which have no sieves attached to them, are used, it is necessary to have a sifting machine. This consists of a hollow octagonal prism rotating on an axis slightly inclined to the horizontal. The phosphate meal enters at the upper end, and, by rotating, gradually works down to the lower end. The flat sides of the octagon have framed sieves, which are fastened by any simple device.

Mixing the Acid and Phosphates.—To blend the acid with the phosphate, a " mixer " is used. The rock phosphate and sulphuric acid are weighed out in appropriate amounts and placed in the mixer. For the purpose of determining the amount of sulphuric acid and rock phosphate that should be used in the mixer, it is necessary for the manufacturer either to know by actual practice the volume of acid consumed by the phosphate in use at the time, or else to calculate the proportions from the result of analysis. Table 18 gives a statement showing the amount of acid of various strengths that is consumed by the different ingredients in the rock phosphates. It will be noticed in Table 18 that iron oxide and alumina consume a large amount of acid in proportion to other materials, a fact which explains why iron and alumina are so little liked by the superphosphate manufacturer. In modern appliances the reservoir for measuring the acid and the weighing machine for weighing the phosphates can be made partially automatic, so that once having been fixed at definite weights and volumes, they will continue to send the materials into the mixer at the correct rate. The mixer itself may be formed according to several different designs. Some of the old-fashioned mixers consist of lead-lined wooden troughs, in which a spirally-grooved core mixes and propels forward the materials as they are delivered into the trough. For small mixers this method works satisfactorily enough, but lead is a soft metal to withstand such rough usage. To deal with several hundredweights of acid phosphate sludge

at a time; larger mixers are constructed of brick, protected by some means from the action of the acid.

TABLE 18.

POUNDS OF ACID CONSUMED BY 100 POUNDS OF ROCK PHOSPHATE FOR EACH PER CENT. OF THE CONSTITUENT STATED.

Specific gravity of acid, D	1·56	1·58	1·60	1·62
Tricalcium phosphate	1·14	1·11	1·09	1·07
Calcium carbonate	1·46	1·43	1·40	1·37
Iron oxide ($\frac{1}{2}$), aluminium oxide ($\frac{1}{2}$)	3·34	3·25	3·19	3·11
Unestimated (CaF_2, NaCl)	0·12	0·11	0·10	0·09

The use of the table can best be explained by an example.

Algerian phosphate.	Acid (D = 1·56)
Calcium phosphate . .	65·0 × 1·14 = 74·2
Oxide of iron and alumina	0·6 × 3·34 = 2·0
Calcium carbonate . .	16·0 × 1·46 = 23·4
Water	5·0
Unestimated . . .	13·4 × 0·12 = 1·6
Pounds of acid for 100 pounds phosphate	101·2

The manufacturer used equal weights so as to leave some insoluble phosphate.

It is now possible to produce bricks having a high degree of resistance towards sulphuric acid, and to manufacture cements which make a satisfactory acid-resisting mortar to join such bricks. There are many well-known brands of these acid-resisting bricks, known as blue brick, metalline, etc., and these are joined together with cements which consist very largely of ground-up bricks of a similar type, together with small quantities of lime and silicate. One particular recipe is ground stone waste passing through a No. 30 sieve, 8 parts; fine Leighton sand, 7 parts; ground blue brick passing through a No. 60 sieve, 2 parts; plaster of Paris, one-eighth part, all mixed intimately together, and subsequently treated with 3 parts of sodium silicate solution with a specific gravity of 1·3. Such a strength of sodium silicate can be made by diluting the strong syrup of sodium silicate

with an equal volume of water. The cement should be used within an hour from mixing, and the finished work heated to about 100° C. (212° F.), for several days, or at a higher temperature for a shorter time. Another recipe consists of 10–100 parts of ground brick or fine sand, mixed with 1 part barium sulphate, to which is added 20–50 parts of sodium silicate of 1·3 specific gravity, that is sufficient to be able to mix the material to a convenient consistency for trowel work. These cements stand the action of sulphuric acid fairly well. The barium sulphate cement sets more slowly than the lime kinds, but it ultimately becomes very hard and resistant to acids. A thinner mixture of barium sulphate, clay and sodium silicate makes a very good wash to rub over the surface of existing and somewhat damaged brickwork, as it penetrates into the cracks, crevices and pores, and fills them up with a meal which resists the action of acid very well.

The metal part of the screw which works inside the mixer can be made from what is commonly known as chemical cast iron, some kinds of which are sufficiently resistant for the purpose. There are now several alloys, such as tantiron, duriron, ironac, etc., which contain about 15 % of silicon, and 85 % of iron, which are very suitable for this purpose. Sometimes vertical mixers of an egg shape are used placed over the dens, in which case the phosphate and acid are fed into the mixer, and blended by beaters inside. These vertical mixers are nearly always made of an acid-resisting iron, and are rather more expensive and more difficult to repair than the older forms. When the phosphate has been ground up fairly fine, and the acid is of reasonable strength, two or three minutes in the mixer is enough. The amount of phosphate used at any time in the mixer depends upon whether the phosphate is rich in carbonate or not. The acid and the phosphate are run into any type of mixer simultaneously, which can either work on the intermittent or the continuous system, according to the method of working. The temperature of the acid used should generally be about 25° C. (77° F.), and its specific gravity a little under

1·6. A certain amount of heat is evolved, chiefly owing to the action of sulphuric acid on calcium carbonate, but the temperature can be regulated to some extent by the degree to which the acid has been diluted. The temperature to which the mass rises will vary, but may occasionally reach 200° C. (400° F.). The results of the heat produced, are that much steam is given off, and the superphosphate is partially dried. After having been mixed for two or three minutes, the sludge is discharged from the mixer into a channel, down which it flows into the dens. It is convenient that this channel should be set at an angle, so that it may work by gravity, but where this is not practicable a screw conveyor must be arranged to help the sludge along.

The dens are brick chambers of any convenient size up to 1000 cub. ft. capacity, to suit the particular factory, and are best built of bricks which resist the action of acids. Unless they are fairly resistant, the bricks gradually crumble, and the den ultimately falls down; this is especially important if any weight is placed upon the bricks at the top, as is very frequent with vertical mixers. With the ordinary type of den, which is a square brick building, the front is composed of loose wooden boards, which are fastened to the front without any special device excepting that of propping them up with other planks. Special doors on hinges give endless trouble, as the material of which the hinges are made becomes corroded and worn. The planks become much damaged by the action of the acids, and it is therefore desirable that they themselves should be protected in some way. Planks made of ordinary deal, or any soft wood, like pine or larch, can be made very highly resistant by dipping into melted naphthalene. Naphthalene at 100° C. (212° F.), penetrates the wood fibres with great ease, and on cooling crystallizes in the spaces between the wood fibres. Painting the planks with sodium silicate solution also helps to preserve them.

During the manufacture of superphosphate, there are given off poisonous gases, consisting of carbon dioxide, hydrofluoric acid, hydrochloric acid, sulphur dioxide and volatile organic compounds. To protect the workmen from

these fumes, the dens are connected with a powerful fan, which sucks the air from the dens and drives it through one or more wash towers. Water is either sprayed into the exhaust gases or allowed to trickle down a column of coke or over boards set on end. Up to the present no use has been found for the condensed gases.

It is necessary now to consider some of the changes that are taking place in the mixer and in the den as the result of the action of sulphuric acid upon the rock phosphates. First of all, as regards the main constituent, calcium phosphate. In the system, phosphoric acid, calcium oxide and water, there is normally a solid phase (see p. 162) consisting of mono and di-calcium phosphates, and a liquid phase consisting of phosphoric acid, water and mono-calcium phosphate. The proportion of free phosphoric acid and di-calcium phosphate in the mixture depends, in practice, upon the quantity of water which is introduced by the sulphuric acid. When increasing quantities of mono-calcium phosphate are dissolved in a given weight of water at a constant temperature, the proportion of free phosphoric acid continually increases, and tends towards a limit in accordance with the equation :

$$2\ CaH_4(PO_4)_2 \rightleftharpoons CaH_4(PO_4)_2 + CaHPO_4 + H_3PO_4$$

Up to the saturation point at 15° C. (59° F.), there is a liquid phase, consisting of water, mono-calcium phosphate and free phosphoric acid, with a solid phase consisting only of di-calcium phosphate, formed by hydrolysis of mono-calcium phosphate. Beyond the saturation point, with increasing quantities of calcium oxide and phosphoric acid, the liquid phase remains unaltered, whilst the solid phase is continually increasing in amount by additions of mono-calcium phosphate. On raising the temperature, the decomposition of the mono-calcium phosphate is increased, whilst the solubility of the di-calcium phosphate is increased at the expense of the solid phase.

Commercial Superphosphates.—Experimental data show that superphosphates may be considered as existing in two given types—those that are normal, and those that

cannot be classed as such. The object of the manure manufacturers is to produce a superphosphate with the correct mechanical properties, which permit of its easy handling and distribution on the field. These properties depend upon the proportion of free phosphoric acid and water present in the finished article. The water content depends upon the amount of water introduced with the sulphuric acid, whilst the amount of free phosphoric acid depends upon the relative proportions of all the interacting substances, and upon the fineness of the solid portion. The ultimate amount of water left in the superphosphate will depend not merely upon the water which is introduced into the mixer, but will also depend inversely upon the amount of water which is evaporated in the subsequent treatment. When the acid is fairly strong, the temperature of the superphosphate will be raised, and if ample ventilation is given, much water will be evaporated. When the rock phosphate contains much carbonate, large volumes of gas are given off and the temperature rises, both of which conditions assist in evaporation of water.

When mineral superphosphates are carefully prepared, they may be considered as belonging to the normal type, but much of the commercial superphosphate does not fall into this group. In practice, in normal superphosphate, the amount of water should not exceed 12 %. In a properly prepared superphosphate, di-calcium phosphate should always be present, and the fraction of phosphoric acid, combined with calcium in the form of di-calcium phosphate, should be equal to that present as free phosphoric acid. The remainder of the soluble phosphoric acid, that is the greater part, is present as mono-calcium phosphate. Mono and di-calcium phosphates are mostly present in the hydrated form, and the calcium sulphate should also have its full amount of water of crystallization. These hydrated salts are formed by secondary reactions in the den.

Superphosphates of defective constitution show a higher percentage of water than 12 %, and contain more than 2 % of free phosphoric acid reckoned as P_2O_5; di-calcium phosphate is either absent, or only

present in small amounts, that is the ratio H_3PO_4 : $CaHPO_4$ is large, say 10 : 1 ; anhydrous forms of mono-calcium and di-calcium phosphate may be present in considerable quantities. Such mixtures show very defective mechanical properties, and may, in extreme cases, be so pasty that they cannot be distributed. A correctly prepared superphosphate should be capable of being kneaded between the fingers without working up like putty. To obtain such desirable properties, the manufacturer must limit the proportion of water and free phosphoric acid. The evaporation of water in the den varies directly with the concentration and temperature of the acid, the temperature of reaction, and the excess of lime over phosphoric acid in the mineral phosphate used. The use of hot acid in the mixer promotes too rapid evaporation before the mass has become well mixed, and it is therefore preferable to keep the temperature down below 30° C. (88° F.), but there are some particular phosphates, such as the Somme phosphates, which many manufacturers prefer to treat with acid at a higher temperature. It is essential that the sludge in the mixer should be kept in a paste-like form for a sufficient length of time, so that it can be uniformly distributed, both in the mixer and in the den.

The concentration of the acid to be used varies with the nature of the mineral phosphates and the moisture that they contain. Many makers prefer to use an acid of a fairly low gravity, 1·57, but such superphosphates are often rather damp. A better practice is to use an acid of a gravity of 1·6, which is very suitable for lumpy phosphates. The result of raising the temperature of the reaction is to increase the concentration of free phosphoric acid in the liquid phase, whilst in the solid phase di-calcium phosphate increases in equal proportion owing to increased decomposition of mono-calcium phosphate. Indeed, mono-calcium phosphate is hydrolyzed in the presence of an excess of sulphuric acid. The duration of mixing should therefore be kept very strictly to the time necessary for complete and uniform admixture which, with good apparatus, is less than half a minute. The

conversion of the phosphoric acid into soluble forms depends on various points, such as the nature of the rock phosphate, its hardness, its structure, the method of grinding and the proportion of fine powder to granular matter. Under modern systems of grinding, superphosphates are prepared which leave 0·5–0·7 % of insoluble calcium phosphate, whereas at one time this proportion exceeded 2 %. It is not uncommon to find some poorly made phosphates of modern manufacture which contain much insoluble phosphate as a result of coarse grinding. On the other hand, excessive fineness of the meal tends to produce undesirable mechanical conditions in the final product; a certain amount of granular structure is necessary. Hard rock phosphates yield products containing more free phosphoric acid than do the more friable phosphates, a result which is partly due to the finer material produced from the hard rock phosphates, and partly due to the fact that the hard rock phosphates are not so easily penetrated by the sulphuric acid.

Many hypotheses have been adopted from time to time to explain the actions proceeding in the mixer and in the den. Where sulphuric acid is used in excess, the reactions probably occur in accordance with the equations :—

(1) $Ca_3P_2O_8 + 3H_2SO_4 + 6H_2O = 3CaSO_4.2H_2O + 2H_3PO_4$

(2) $Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O = 5CaSO_4.2H_2O + 3H_3PO_4 + HF$

(3) $Ca_5(PO_4)_3OH + 5H_2SO_4 + 9H_2O = 5CaSO_4.2H_2O + 3H_3PO_4$

In equation (2) F may be replaced by Cl or organic group. If the amount of sulphuric acid used is insufficient to completely decompose rock phosphate, the reaction is generally supposed to take place in accordance with the following equations :—

(4) $Ca_3P_2O_8 + 2H_2SO_4 + 5H_2O = 2CaSO_4.2H_2O + CaH_4P_2O_8.H_2O$

(5) $2Ca_5(PO_4)_3F + 7H_2SO_4 + 17H_2O = 7CaSO_4.2H_2O + 3CaH_4P_2O_8.H_2O + 2HF$

(6) $2Ca_5(PO_4)_3OH + 7H_2SO_4 + 15H_2O = 7CaSO_4.2H_2O + 3CaH_4P_2O_8.H_2O$

According to more modern ideas, the reaction is supposed to take place in two stages, first according to the equation used for excessive sulphuric acid, *i.e.* (1), (2) or (3), and then the free phosphoric acid reacts according to the following equations :—

(7) $4H_3PO_4 + Ca_3P_2O_8 + 3H_2O = 3CaH_4P_2O_8 . H_2O$
(8) $7H_3PO_4 + Ca_5(PO_4)_3F + 5H_2O = 5CaH_4P_2O_8 . H_2O + HF$
(9) $7H_3PO_4 + Ca_5(PO_4)_3OH + 4H_2O = 5CaH_4P_2O_8 . H_2O$

Observations under working conditions show that the following equation represents better the main reaction in practice :—

(10) $5Ca_3P_2O_8 + 11H_2SO_4 + 26H_2O$
$= 4CaH_4P_2O_8 . H_2O + 2H_3PO_4 + 11CaSO_4 . 2H_2O$

The free phosphoric acid reacts on more phosphate to form a little di-calcium phosphate, and mono-calcium phosphate decomposes to a little di-calcium phosphate and free phosphoric acid. Excess of acid reduces the amount of di-calcium phosphate.

Calcium Carbonate.—The equations given to represent the action of sulphuric acid on calcium phosphate require modification to include the numerous impurities, such as calcium carbonate, magnesium carbonate, etc., which absorb sulphuric acid. It is hardly correct to describe calcium carbonate altogether as an impurity in this case, since without some calcium carbonate the resulting superphosphate would be very pasty and unsuitable for use. In treating phosphates with sulphuric acid, it is the carbonates of lime and magnesia that are attacked first. Carbonate of lime is invariably present, though carbonate of magnesia is also met with in a few cases. The decomposition of calcium carbonate by sulphuric acid forms, in the first instance, anhydrous calcium sulphate, and, later on, the hydrated form, gypsum, and is the main cause of the increased temperature of the mass. At the same time, much carbon dioxide is evolved, to the great advantage of the mechanical condition of the finished superphosphate. Phosphates, which contain little carbonate of lime, heat only slowly and slightly in contact

with acid, the solution of phosphate is very slow, and the product is difficult to dry. Where such a material is being used, it is better to mix it with one of the poor grade rock phosphates containing higher proportions of carbonate of lime. The reactions of calcium carbonate with sulphuric acid and magnesium carbonate are given in the equations :—

$$CaCO_3 + H_2SO_4 + H_2O = CaSO_4.2H_2O + CO_2$$
$$MgCO_3 + H_2SO_4 + 6H_2O = MgSO_4.7H_2O + CO_2$$

Magnesium sulphate can also crystallize with 6 molecules of water. Occasionally, but very rarely, magnesia is met with as a phosphate. The acid phosphate of magnesia is not deliquescent, like the corresponding calcium compound, nor is it at all readily decomposed by water. Up to 5 % of calcium carbonate may be regarded as a beneficial amount ; greater quantities merely absorb sulphuric acid to little purpose, add to the weight of the resulting material, and cost money in freight and cartage to no ultimate advantage.

Fluorine.—Many of the phosphates contain fluorine, either as calcium fluoride or as apatite. In the latter case, reaction takes place as described on p. 145 in equations (2), (5) and (8). Should any calcium fluoride be present, reaction takes place according to the equation :—

$$CaF_2 + H_2SO_4 + 2H_2O = CaSO_4.2H_2O + 2HF$$

The ordinary rock phosphates almost invariably contain a certain amount of earthy material, so that there is a fair amount of silica present. In the absence of water, hydrofluoric acid acts upon silica according to the following equation :—

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

but the silicon tetrafluoride so produced reacts with water, according to the following equation :—

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$$

Hydrofluoric acid is not merely capable of acting upon silica, but also upon complex silicates, and will attack the brickwork of the den if it has not already obtained sufficient silica from the superphosphate. As the mass by its heat

is always giving off steam, the latter and silicon tetrafluoride will often meet where the gases escape, and it is therefore very common to see in the flues, in the doors and any odd corners of the den, large masses of sponge-like silica, which have been produced by these chemical changes. Different observers discover different proportions between the fluorine that escapes and that which remains. It is only to be expected that there should be this great difference, as the water present and the heat evolved will influence these proportions considerably. Silicates of lime and alumina occur in some of the rock phosphates, the former are decomposed by either sulphuric or phosphoric acid, but only somewhat slowly. Part of the reversion alluded to on p. 154 is possibly due to some such slow reaction taking place.

Other Halogens.—Along with true apatite, there are present in the rock phosphates some bodies of analogous composition, in which chlorine, iodine or hydroxyl takes the place of fluorine. Chlorine, if present, is evolved as hydrochloric acid, and passes off with the remaining gases into the washer. Iodine may also be present in traces, when it is given off as hydriodic acid. As the latter is partly oxidized by atmospheric oxygen, small quantities of free iodine are occasionally liberated, and give a slight violet tinge to the effluent gas.

Iron and Alumina.—The presence of oxides of iron and alumina in the raw phosphates produces many objectionable results, so much so that in certain cases raw phosphates become quite unsuitable for superphosphate manufacture. Very often the iron is present as ferric phosphate, although occasionally pyrites may be found, as in the Tennessee phosphates. Decomposition between the sulphuric acid and the phosphates may take place according to the following equations :—

(1) $3FePO_4 + 3H_2SO_4 = FeH_6P_2O_8 + Fe_2(SO_4)_3$

(2) $2FePO_4 + 3H_2SO_4 = 2H_3PO_4 + Fe_2(SO_4)_3$

If the iron present is equal to less than 2 % of oxide of iron in the raw phosphate, little injury is done, because to that degree phosphate of iron will remain in solution. The ferric

sulphate produced by interaction with ferric phosphate and sulphuric acid, is, however, capable of decomposing monocalcium phosphate, with the production of ferric phosphate. Ferric phosphate commonly occurs in two forms, the hydrated form and the dehydrated form. If the amount of water present is insufficient, calcium sulphate, during hydration to gypsum, may take the needed water from the ferric phosphate, which is then much more difficult to attack by acid. Alumina compounds usually react somewhat slowly, and are hence distinctly objectionable, since they tend towards retrogression.

Organic Matter.—The smell alluded to on p. 27 which is given out when some rock phosphates are ground is also produced when these phosphates are acted upon by sulphuric acid. This smell is due to the organic matter contained in the rock phosphates. No serious importance need be attached to this volatile substance; even if the organic matter becomes charred by sulphuric acid in the process of mixing, no diminished fertilizing value need be feared.

Emptying the Den.—Much of the work of emptying the den is still carried out by hand labour. After the dens have been filled from the mixer to perhaps two-thirds of their height, the mass of acid and phosphate rises to the top of the den in the course of an hour or two. Owing to the heat produced by the reaction, both steam and gas are given off, which are then drawn away by a fan; but the mass, although now dry and crumbly, is very hot and continues to give off steam. The work involved in removing the superphosphate from the den is both arduous and unpleasant. One man removes the stuff from the den with a pick, two men fill barrows, and a fourth or even a fifth man is needed to wheel the superphosphate away by a plank and tilt it on the heap. Where works are slightly better equipped, there is generally a cup elevator placed nearly in front of the den, and the material is put straight away into the cups. Where the manufacturer makes a great point of producing a good, dry superphosphate, it is not uncommon for the material to be passed through riddles at once, and as it passes through

the riddles it is dusted over with a finely powdered rock phosphate. The object of this riddling and dusting is to obtain the material in a fine, dry condition, suitable for sowing.

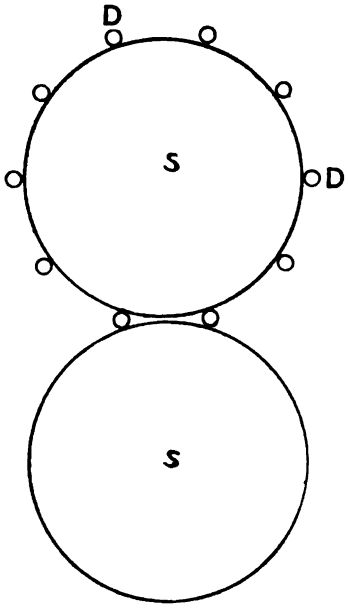

FIG. 8.—Section of dusted particles.

SS are two particles of sticky superphosphate, very highly magnified.

DD are the dust particles which adhere to the sticky surface, but prevent the sticky superphosphate particles from coalescing. The diagram is drawn to a scale of about ½ % of dust particles, assuming them to be evenly distributed.

The advantage of dusting a very small quantity, perhaps only ½ %, of rock phosphate is partly chemical, but very largely a purely physical one. In Fig. 8 is shown the manner in which large damp particles are prevented from uniting by the interposition of small dry particles equal to one-half of a per cent. of the total mass. This action can be seen very well from the way in which dusty globules of mercury do not coalesce. As the particles do not roll on one another without limit seeking to coalesce, it is only necessary to reduce the chance of coalescing. Hence a small percentage will serve the purpose. On the other hand, the dust grains are not evenly distributed, and therefore many are wasted. Hence more dust is needed. The two errors tend to balance one another. Moreover, many of the particles of dust may be nearer one-thousandth of an inch in diameter. Hence, in practice, small proportions of dust are effective, if skilfully used. There is, however, great difficulty in anything approaching even distribution. Very minute particles of a substance not acted on by the liquid phase of superphosphate would be almost equally effective, but are not used in practice.

It would not be wise to attempt to be too successful in dusting, since the superphosphate needs to become wetted after application to the soil. With a moderate amount of care, a superphosphate "dusted" in this way will stand a considerable amount of pressure without adhering to the drill or other implement used for distribution on the soil.

During the operation of removing from the den, a fair amount of drying takes place. It is therefore desirable that plenty of air should obtain access to the substance while it is still hot. Where the work is carried out by hand labour, and the meal is quickly and immediately riddled, much drying automatically takes place. It is very important, at this stage, that the superphosphate should be pressed together as little as possible, otherwise it forms a sticky mass, which cannot be reconverted to a fine dry condition. In some works the workmen are provided with respirators to prevent them breathing any poisonous gas, but where the dens are properly constructed with good fans, and the front of the den is placed in a situation where there is a good natural draught, there is no necessity for this precaution. The works should be so designed that the front of the den, screening floor and cup elevator are all situated where there is usually a draught, as by these means the danger of asphyxiating fumes can be removed without any measurable effort or expense.

As a rule, it is possible to begin to extract the superphosphate from the den in 1–2 hours from the time when it was filled, but it is not desirable to work at such a pace, as the reaction is by no means completely over, and removing superphosphate from the den before the reaction is complete is bad practice if the material is chilled. The reaction is therefore still further delayed, and the probability of turning the superphosphate into a sticky mass is much increased. Manufacturers, therefore, should have several dens, so that they may not be compelled to empty them too frequently. Forced by the large amount of labour needed for extracting the superphosphate, and the expensive character of the work, manufacturers have attempted to design

mechanical appliances for extracting the material. Improvements have been made by having false bottoms which allow the material to drop out on to a conveyer. This method still necessitates a great deal of hand work. More complete arrangements are employed in some of the modern forms of mechanical dens. These may be divided into two types, one in which a revolving cutter is pushed into the den, and the other in which the den itself moves forward against rotating knives. These modern dens must therefore be of a cylindrical form, and consequently do not possess the capacity for the same amount of floor space that the ordinary old-fashioned cubical brick den possesses. Where the den is fixed, the cutting knives advance in a spiral into it, and near the end of their run a great strain is placed upon the spiral mechanism propelling the cutting blades into the den. From the engineering point of view it is better to have the den itself moving; this design gives a less complicated movement to the cutting blades. Where the den moves, simplification is generally effected by having a cylindrical den moving forwards on two screws placed near the ground. The knife blades are set spinning, and the den moves forwards against them. The superphosphate removed from the den is then immediately conveyed to an ordinary cup elevator and passed through riddles. The whole of the cup elevator should in this case be enclosed, and connected with the fans, so as to draw away the steam and poisonous vapours. Not merely does the current of air draw away acid fumes, but it also dries the superphosphate. In any case of removing superphosphate, great care must be taken not to compress it too much, otherwise it becomes sticky. It is for this reason that dusting the material over at an early stage is advisable. Some of the machines constructed for excavating superphosphate also make arrangements for dusting on some fine powder.

In certain cases some of the superphosphates are artificially dried. This artificial drying may be conducted by the simple plan of spreading the superphosphate on a hot stone floor, which is heated by some waste flue gas. If

floor space can be afforded, this method of drying is quite efficient, but much labour is spent in spreading. Special machines with a rotary movement are also constructed for drying superphosphate in a continuous manner. The removal of water modifies the relationship between the four forms of phosphorus in the superphosphate, viz. between the tri-calcium, di-calcium and mono-calcium phosphates and the free phosphoric acid. In the case of well-made superphosphate, the amount of free phosphoric acid is reduced by drying, since, owing to the removal of water, free phosphoric acid reacts with di-calcium phosphate with the formation of mono-calcium phosphate. By careful drying, the percentage of water soluble phosphate is raised, and the mechanical condition is improved. In the case of badly made superphosphate which contains large quantities of free phosphoric acid and in which the physical condition is bad, the removal of water during drying is very slow, and sometimes only superficial; owing to the relative absence of di-calcium phosphate, the reduction of free phosphoric acid by drying is very slight, so that actually, after the removal of water, the free phosphoric acid may become slightly higher, instead of slightly lower, due to the general concentration of all the constituents. Consequently, badly made superphosphates do not benefit much by artificial systems of drying.

Some artificial drying of superphosphates may be carried out by admixture with other materials. The other materials used may be small amounts of rock phosphates, which have been dusted in the way described on p. 150, or gypsum may be added, merely as a means of absorbing liquor rather than as an agent of desiccation. Drying superphosphates by admixture is more commonly carried out in the general process of making compound manures, described on p. 179. Where superphosphates are overheated in the effort to dry them, the phosphoric acid may be dehydrated. If phosphoric acid be heated at 105° C. (221° F.), for three hours, as much as 10% may be converted into pyro-phosphoric acid, whilst if heated to 200° C. (392° F.), most of the ortho-phosphoric acid will have been dried and changed

into pyro-phosphoric acid; some will have gone as far as meta-phosphoric acid. Unless such an overheated superphosphate so obtained is boiled at some period of its treatment with acid during analysis in the laboratory, the analysis will be misleading, since pyro- and meta-phosphates do not give the same precipitates as ortho-phosphates. Meta- and pyro-phosphates are not immediately absorbed by plants, but they revert to ortho-phosphoric acid in the soil at a sufficient rate to become fully utilized by crops.

Retrogression.—Superphosphate keeps very well from one season to another, provided the phosphate from which it was made does not contain more than 2 % of oxide of iron and alumina. Retrogression is the result of many causes, some chemical and some physical. The heat and pressure engendered in the heap of superphosphate are important in increasing the rate at which retrogression takes place. The granules, of which superphosphate consists, may adhere on contact, when pressure is applied, unless the granules have been dusted as described on p. 150. As the depth of the layer, in which superphosphate is stored, increases, the substance becomes compressed by its own weight, so that finally the particles may be compacted together. These changes are more rapid in moist, hot superphosphate than in superphosphate which has been dried and cooled.

The crystallization of calcium sulphate is by no means complete when the den is emptied hastily, and it continues in the heap. Mono-calcium phosphate also reacts with the sulphate of iron and alumina in the heap, producing retrogression and bad physical conditions. Pressure in the heap is therefore one of the evils to be avoided as far as possible. It is consequently not desirable to pile the superphosphate in large heaps until it has been made many hours. The method of drying superphosphate by spreading in a thin layer on a hot plate has the advantage that it entirely prevents pressure taking place before the superphosphate has reached a stage when it is less likely to revert. The degree to which superphosphate may retrograde may be discovered by artificial pressure. A pressure of about 4

atmospheres, applied by weight and lever, will show in the course of a few days what retrogression may be expected in any particular sample of manure. It is, however, rare to find a superphosphate that retrogrades more than 1–2 % in the course of twelve months, and it is not easy to obtain consignments of superphosphates which are constant in composition to that extent.

A Phosphatic Nitrate has been produced in Sweden by acting upon mineral phosphate with the weak nitric acid produced by an electric furnace. To prevent overloading the manure with nitrogen, it is only possible to use so little nitric acid that much of the mineral phosphate remains undissolved. Experiments showed that a large proportion of undissolved phosphates was no disadvantage when used for growing oats. (Compare p. 187.)

Basic Superphosphate.—In the early days of the manufacture of superphosphate, phosphates were often only partially dissolved, and as much as 8–10 % of undissolved phosphate was retained. It was easy to make an excellent dry fertilizer by such methods, but with the endeavour to make the most out of rock phosphates, the amount of insoluble phosphate left behind has been reduced to 1 % or 2 %. As time went on, superphosphate became damper and more acid, and difficulties arose in its distribution in the ordinary corn drill. Improvements in distributing machines overcame this difficulty to some extent, and greater skill in manufacture, as described above, also tended to produce drier superphosphates; at last an alternative scheme was evolved to treat damp and unsatisfactory superphosphates with a small quantity of lime, so as to obtain them in a drier condition. About 85 parts of superphosphate were thoroughly mixed with 15 parts of good slaked lime, and allowed to remain for at least 24 hours. By these means a fertilizer was obtained which contained very little phosphoric acid soluble in water; nevertheless most of the phosphate present was easily soluble in very weak solutions of citric acid or ammonium citrate. The solubility, as tested by any method, exceeded that of the basic slag. The mechanical

condition of basic superphosphate is excellent, as it is a dry, fine powder, easily distributed either by hand or machine. The drill is never clogged, and it does not adhere to the hand in hot, damp weather. The material is, however, very bulky, occupying from two to three times the space occupied by the same weight of basic slag. Basic superphosphate is particularly advantageous for use with turnips or other crops which do badly under acid conditions. This mixture has not come into much favour, because it is somewhat expensive to produce; if both superphosphate and lime are necessary, it would be more beneficial to apply the lime to one crop of the rotation and the superphosphate to another. Such double distribution may entail slight extra expense in actual application to the field, but it would prove more profitable. During the war period there was a time when the supply of sulphuric acid was very short, so that efforts were made to economize its use by treating superphosphate with finely-ground rock phosphates. With such a mixture, much of the phosphate ceased to be soluble in water, but was soluble in weak acids or ammonium citrate. With the return of plentiful supplies of sulphuric acid, this variety of phosphatic manure has again fallen into the background. Actual experimental trials to compare basic superphosphate against ordinary superphosphate have not shown any particular advantage. It is more economical and convenient to use rock phosphate than to use lime for drying superphosphate, see p. 187.

"Tetraphosphate" of Lime.—The cost of production of superphosphate has led to the commercial development of the so-called "tetraphosphate" of lime, invented by Professor Stoppani in 1911. It is made by heating finely-ground natural phosphates with 5–6 % of a mixture of calcium, magnesium and sodium carbonates to a temperature of between 600° and 700° C. (1100° and 1300° F.). The calcined mass is moistened, and then diluted with earth or sand, until its phosphate content is reduced to about 40 % tri-calcium phosphate. This material is manufactured in Italy, at Luxor on the Nile, and at Kosseir on the Red Sea

Littoral. It is said to be a very satisfactory fertilizer, but there is no real evidence to show that it possesses any superiority to other phosphates. It can easily be understood that, if the material is applied to land that is lacking in lime, it may have proved superior to superphosphate, or, that where sodium and magnesium are lacking, its advantage may be due to the presence of some of the sodium or magnesium compounds. Until the matter has been more fully dealt with, the production of this article must be looked upon as an enterprise of doubtful value, since the original ground natural phosphates, without any treatment at all, are quite capable of producing satisfactory results on soils very deficient in phosphates. Other similar attempts have been made to calcine rock phosphates, with the idea that they would then form some special new compounds, supposed to be represented by the formula $Ca_4P_2O_9$. Little experimental evidence is available to suggest that the treatment has rendered the material of much greater value than before. A rock phosphate containing large proportions of calcium carbonate might be economically improved by calcining, if only for the reason that the loss of moisture and carbonic acid would save freightage charges. Calcining also mechanically disintegrates the mineral, especially when much carbon dioxide is given off in the process.

Precipitated Bone Phosphate.—For the manufacture of certain classes of glue and gelatine, bones are treated with hydrochloric acid. It is preferable that the bones should first of all be extracted with benzine, to obtain them free from fat, as described on p. 73, otherwise the acid acts somewhat slowly. By acting upon extracted bones with hydrochloric acid, the whole of the phosphoric acid contained can be dissolved, leaving the gelatinous substance behind. The equation representing this change is :—$Ca_3P_2O_8 + 4HCl = CaH_4P_2O_8 + 2CaCl_2$. As the mono-calcium phosphate is not perfectly stable in presence of water a slight excess of hydrochloric acid must be used. In the actual course of manufacture, the bones are placed in a wooden vat fitted with a mechanical agitator; where the bones are

coarsely ground, a mechanical agitator is not absolutely necessary. After soaking until the bones have become semi-transparent, the solution is run off from a tap at the bottom of the vat, and the residual gelatinous matter is washed with weak hydrochloric acid of about 4 % strength. The weak acid after use for washing is retained for diluting the hydrochloric acid used in preliminary extractions. The strength of the acid used for the first extraction of the bones varies according to the practice in different works from about 7–12 %. The amount of hydrochloric acid used should be as little in excess as possible. When the bones are very finely ground, and an agitator is used, a solution can be effected in 10–15 minutes, but with larger bones the time is correspondingly lengthened. The solution, which should contain very little free hydrochloric acid, is transferred to a lead-lined vat, in which it is neutralized by milk of lime. Endeavours should be made to approximate to a precipitate having the composition of di-calcium phosphate, but some slight excess of lime must be used, so that the resulting material is a mixture of di- and tri-calcium phosphates, produced according to the equations :—

$$CaH_4(PO_4)_2.H_2O + Ca(OH)_2 + H_2O = Ca_2H_2(PO_4)_2.4H_2O$$
$$CaH_4(PO_4)_2.H_2O + 2Ca(OH)_2 = Ca_3P_2O_8 + 5H_2O$$

It is desirable that there should be sufficient chemical control at this stage to prevent an excess of lime being used; samples can be taken from the vat, filtered and tested for soluble phosphates. Traces of soluble phosphates are certain to remain in solution unless excess of lime is used, hence a compromise must be effected. The muddy liquor is then run through a filter press, and the calcium chloride washed out. It is important that the washing should be fairly efficient. The cakes are then dried at a low temperature, when a fine friable powder results, containing from 30 to 40 % of phosphoric acid. The meal approximates to a mixture of equal amounts of di- and tri-calcium phosphates. Precipitated bone phosphate is very easily soluble in the weakest citric acid solution, or in ammonium citrate. The meal is

practically neutral, and can therefore be applied even to germinating seeds or young tender leaves without injury. It makes an excellent manure for a turnip crop, as it is not in any degree acid, but supplies sufficient lime and phosphates in an easily available form. Farmers not infrequently find that this is a convenient material to dust on to young turnip plants to ward off attacks by the turnip fly (see p. 246).

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Section IV.—POTASSIUM FERTILIZERS

Blast Furnace Potash.—The blast furnace dust referred to on p. 61 can be used directly as a manure, or it can be worked up for concentration and purification. Much of the blast furnace dust produced up to the present has been used as the raw material for the preparation of potassium compounds such as chlorate, permanganate, etc. Blast furnace dust provides a very excellent source of high-grade potassium chloride. Pure salts can be prepared more easily from blast furnace dust than from mineral potash compounds, consequently it is highly probable that blast furnace potash will be largely used for industrial purposes; but just as there are large residues from the potash minerals, so doubtless there will be residues from dusts also. Where sodium chloride is added to the furnace for the purpose of increasing the yield of potash, most of the potash is obtained as chloride, and can be easily washed out of the dust by water, and recovered from solution by crystallization. It will be necessary to set up central factories to deal with this work efficiently and make Great Britain self-supporting.

Potassium Sulphate from Cement.—The potash content of clays and shales suitable for cement manufacture may be as high as 2½ %. By adding fluorspar equal to 80 % of the total potash present, 90 % of the potash is volatilized in a cement kiln as potassium fluoride. The presence of sulphur in the fuel produces sulphuric acid, which reacts with the potassium fluoride and lime compounds present to form calcium fluoride and potassium sulphate according to the equation $2KF + CaSO_4 = CaF_2 + K_2SO_4$. On washing the resulting dust with water, potassium sulphate dissolves and calcium fluoride is left in an insoluble form. By filtering and washing at temperatures of 85° C. (185° F.), or slightly over, the double salt $CaSO_4.K_2SO_4.H_2O$ is prevented

from forming, and most of the potash is returned as soluble potassium sulphate, whilst nearly all the fluorine is recovered in the filter press as a cake of calcium fluoride, mixed with calcium sulphate. Nearly all the fluorine used can be returned to the furnace in the form of this cake.

About 90 % of all the potash present in the materials is volatilized, from which must be subtracted about 10 % lost in the collectors and 5 % lost in washing. Hence about three-quarters of all the potash in the materials is recovered as potassium sulphate. Potassium sulphate is a more valuable salt for fertilizing purposes than potassium chloride and fetches a higher price.

The Manufacture of Pure Salts from Potash Minerals.—Before considering the special case of the manufacture of commercially pure specimens of the more important potassium salts, it is necessary to discuss some of the general properties of salts in aqueous solution. All substances are soluble to some slight extent in water, but in many cases the amount dissolved is so minute that it may be neglected, and it is therefore common to classify salts as soluble, sparingly soluble and insoluble in water. In the case of every salt there is a maximum quantity which can be dissolved at any particular temperature, but this quantity varies when the temperature is altered, usually increasing with the temperature. In some particular cases, such as that of potassium chloride, the solubility increases step by step with the temperature, but in general the solubility of salts increases with increasing pace as the temperature rises. That is to say, if the solubilities be plotted on squared paper with reference to the temperature, the equation to the curve in the case of potassium chloride is of the form $S = a + bt$, where S represents solubility and t represents temperature. For most salts, a further figure of ct^2 must be added, and perhaps occasionally even t^3 takes part in the equation. The solubility of sodium chloride is expressed on squared paper as an almost straight line. Temperature has, in this last case, very little effect on the solubility, which is nearly constant from 0°–100° C. (32°–212° F.). The

curve for potassium sulphate is only very slightly curved, being almost a straight line like potassium chloride. Magnesium sulphate, another constituent of the potassium manures, exhibits very slight curvature, although the solubility rises steadily with the temperature.

The action of water on a solid is, in the first place, to liberate those molecules with which it comes into contact, and allow them to distribute themselves equally throughout the liquid, until the whole of the salt is dissolved. It follows that the maximum solubility depends upon the exact nature of the solid present; when a salt crystallizes in two different forms, the solubility is almost always different in the two cases; also, the solubility of an anhydrous salt is different from that of its hydrates. Recognition of the principle, that the solubility depends upon the degree of hydration of the salt, has supplied the explanation of broken curves when solubilities are plotted; the break in the curve generally being due to a change in the degree of hydration of the salt separating out at that temperature. The examination of the behaviour of a solid to water is of great importance in the study of the various hydrates formed by the salt. In investigations into the conditions of equilibrium of various systems of solids and liquids, each of the chemical substances present is called a "component" of the system, and each uniform solid or liquid present is termed a "phase." The state of equilibrium in such a system is fully defined when the three variable factors, temperature, pressure and concentration, are known. These three are not always independent of one another, since in many systems when one is fixed the others can be calculated. When it is only necessary to fix one of the three factors in order to have a fully defined state of equilibrium, such a system is said to have only one degree of freedom, but some systems have no degrees of freedom, whilst others have more than one. It has been found that the number of degrees of freedom depends entirely on the number of components and phases which are present.

The general law known as the "Phase Rule," states that in any system which is in equilibrium, the number

of degrees of freedom may be calculated by adding 2 to the number of components, and subtracting the number of phases. For example, in the simple case of water being in equilibrium with water vapour, there is one component and two phases, therefore, according to the phase rule, the number of degrees of freedom will be 1 + 2 − 2, *i.e.* there is only one degree of freedom. If any single change takes place, such as a rise in temperature, only one thing can happen, namely, that there is less liquid water and more water vapour. If we take the case of a salt in solution, the components are salt and water, and the phases are solid salt, liquid water and water vapour. Again, therefore, there is only one degree of freedom, and by raising the temperature, as a rule solid salt goes into solution, the solution becomes stronger, and the amount of water vapour usually increases. In the special case of such a salt as sodium sulphate, having two different crystallized salts, one anhydrous and one hydrated, there are up to a temperature of 32½° C. three phases, solid hydrated sodium sulphate, containing 10 molecules of water of crystallization, the liquid solution, and gaseous water vapour. As there are, therefore, two components and three phases, there is one degree of freedom, and the result of raising the temperature is to increase the amount of salt in solution. When, however, the temperature of 32½° C. is reached, both the hydrated sodium sulphate and the anhydrous sodium sulphate can exist in the presence of water, and therefore there are now four phases, which, according to the phase rule, will not allow any degree of freedom at all. Hence the temperature cannot be altered from 32½° C. without one of the phases disappearing, that is to say, above 32½° the hydrated sodium sulphate disappears, and below 32½° the anhydrous salt disappears. The same principles apply to many of the hydrated salts referred to in the following details of the practical manufacture of pure salts.

Double Salts.—The formation of a double salt from two single salts dissolved in water depends largely upon the temperature. In some cases the double salt can only exist below a certain temperature, but in others it is only formed

above certain temperatures. When equivalent amounts of hydrated sodium sulphate, Na_2SO_4, $10H_2O$, and hydrated magnesium sulphate, $MgSO_4$, $7H_2O$, are treated with a small quantity of water at 15° C. (59° F.) a solution is obtained which is saturated with both these salts, and is in equilibrium with the solid present. At 22° C. (72° F.), there occurs a transition point for the mixture of these salts and the double compound $Na_2SO_4 . MgSO_4 . 4H_2O$, and a certain amount of that double salt is formed. When the temperature rises above 22° C. the single salts continue to dissolve, but the less soluble double compound separates out. The whole of the solid is not immediately converted into the double salt, because magnesium sulphate is more soluble than sodium sulphate, and the solid present is a mixture of sodium sulphate and the double compound. After rising to 25° C. (77° F.) the solid double compound is left with the saturated solution, which contains both sodium and magnesium sulphates. The temperature from 22° to 25° C. is called the transition interval. Carnallite, $KCl . MgCl_2 . 6H_2O$, is completely decomposed by water at 167° C. (335° F.) into the chlorides of magnesium and potassium. It is also partly decomposed at all temperatures below this with the separation of potassium chloride, so that a pure saturated solution of carnallite in water cannot be prepared at ordinary temperatures. The alums, on the other hand, are much more stable in the presence of their solutions, and ordinary potash alum is stable up to a temperature of 92½° C. (200° F.).

Super-saturated Salts.—A clear saturated solution of a salt, if allowed to cool quietly in a closed vessel, may fail to deposit crystals when the solution contains more salt than necessary to make a saturated solution at that temperature ; under such conditions the solution is said to be supersaturated. If, however, a small crystal of the same salt is added, rapid crystallization occurs, generally accompanied by a rapid rise in temperature, and the solution becomes exactly saturated at the temperature prevailing. In the chemical manufacture of pure salts by means of crystallization, super-

saturation may often prevail for a limited period, but as a rule the vessels and implements used contain the crystals necessary to promote crystallization. Rapid movement with paddles assists the crystallization of super-saturated solutions in the presence of those crystals on which the salts in solution can grow. Many salts, which ordinarily are not expected to form super-saturated solutions, may fai to crystallize until cooled well below the temperature at which separation of solid should occur. By the introduction of small quantities of solid crystals and by rapidly stirring the solidifying mass, time may frequently be saved in many crystallizing operations. Where many miscellaneous salts are present in solution, the purity of the crystals separated out may often be largely improved by obtaining such a thorough mixture of crystal and mother liquor that there is only one substance that will crystallize out; on the other hand, should admixture be very imperfect, there is a much greater probability of one substance crystallizing out in one part of the crystallizing vat, and some other salt crystallizing out in another portion. A finer product, both as regards size of grain and quality, can often be obtained by the methods of "seeding" and agitation.

The Manufacture of Potassium Chloride.—The raw material for the manufacture of potassium chloride is sometimes obtained from sylvine, a mixed salt of potassium chloride and sodium chloride. When a saturated solution of sylvine, made at a high temperature, cools down, nothing but potassium chloride crystallizes out. For manufacturing purposes, a solution of sylvine is made at the boiling point, cleared by subsidence, and allowed to crystallize. The crude potassium chloride first obtained can be brought up to 98 % of potassium chloride by washing. From the mother liquor, sodium chloride can be separated out by concentration when sodium chloride crystallizes out near the boiling temperature. The mother liquor from this separation, after cooling down again, deposits more potassium chloride. Again, the mother liquor may be used to dissolve fresh sylvine, when, since the solution is already nearly saturated with sodium chloride, potassium chloride alone dissolves.

The manufacture of potassium chloride is chiefly carried out by re-crystallization from crude carnallite, which is a more difficult process. The composition of crude carnallite is shown in Table 19.

TABLE 19.

COMPOSITION OF CRUDE CARNALLITE.

	Per cent.
Potassium chloride	16
Sodium chloride	21
Magnesium chloride	21
Magnesium sulphate	13
Water..	26

The remaining 2 or 3 % consists of traces of insoluble matter, calcium chloride and a little bromine. The true mineral carnallite contains no sodium at all, but consists of potassium chloride and magnesium chloride only. True carnallite is unstable in the presence of much water, even at a low temperature, and is decomposed into a magma of very fine crystals of potassium chloride and a solution of magnesium chloride with a little potassium chloride in solution. When the solution is heated a much larger quantity of potassium chloride is dissolved, and on cooling the latter salt separates out in large crystals, so long as the amount of magnesium chloride in solution is not more than three times that of the potassium chloride. When this proportion is exceeded, the liquor deposits carnallite. Sodium chloride is much less soluble in hot magnesium chloride solution than potassium chloride, consequently much is left behind in the insoluble form.

The first operation in practice consists in dissolving the crude carnallite, which is usually treated with waste liquors obtained later in the process. The carnallite should be treated as quickly as possible, so that unnecessary solution of sodium chloride is avoided. Most works use the hot liquors at the ordinary atmospheric pressure, or very little above it, with mechanical agitation. With high pressures much more sodium chloride dissolves, and with finely powdered material the same difficulties arise as in treating the fine materials in the manufacture of sodium nitrate described on

p. 94. The liquor that is used for dissolving the carnallite comes from various sources, and consists of washings from the final potassium chloride and other mother liquors. This liquor is run into the dissolver, and steam is injected till the liquid begins to boil, and then the crude carnallite is introduced. The specific gravity is kept at about 1·3, so as to obtain a maximum separation of potassium chloride. The operation of dissolving only takes about half an hour.

The solution now has to be clarified by allowing it to rest for an hour or two in special vessels. This clarification may be assisted by sprinkling on the surface a little milk of lime. As in the case of the manufacture of nitrate of soda, if large lumps are employed it is necessary to have a second boiling. The ordinary liquids passing away for crystallization contain about 10 % of potassium chloride, 5 % of sodium chloride and 20 % of magnesium chloride, with only a small quantity of other salts. The waste carnallite contains about 3 % of potassium chloride, 50 % of sodium chloride and 30 % of magnesium chloride. This residue has been used to fill up the old workings in the mines.

The crystallizing vessels, into which the liquors are run, are wrought-iron tanks of about 300 cub. ft. capacity, with bottoms slanting a little to one side, where there is a plug for running off the mother liquor. Arrangements are generally made for shutters to keep air away from the vessels and to prevent too rapid cooling; when rapid cooling takes place the crystals are small and slimy. The salt first precipitated carries down some materials in suspension, and is usually not so pure as subsequent salts. The bottom salts contain about 55 % of potassium chloride and 30 % of sodium chloride; the side salts contain about 60 % of potassium chloride and 25 % of sodium chloride. The mother liquor that is drawn away from the crystallizing tanks still contains about 20 % of the total potassium chloride, but a portion is used to dissolve fresh crude salts and the remainder is concentrated by evaporation, until on cooling nearly the whole of the potassium chloride present is recovered as artificial carnallite. The concentration in a modern plant is usually

carried out in vacuum pans. The finished salts are washed with water and the wash water utilized for dissolving the crude salts; even then the washed salts still contain a fair amount of sodium chloride. After the crystallization of the artificial carnallite, the liquors running away contain very little potassium chloride, but large amounts of magnesium chloride.

The Purification of Crude Potassium Chloride.—The crude material is washed at a low temperature, whereby some sodium chloride and magnesium chloride wash out. The washing takes place in iron vessels, provided with false bottoms, on which the salts rest, and water is sprinkled on. The washing operation is not practical unless the crude salts contain more than 50 % of potassium chloride. The resulting salts still contain a considerable quantity of water, which is removed by drying. Many systems of drying result in some crusts being formed, which have a different composition from the main part of the crystals. By these means various grades of salts from 80 to 98 % of potassium chloride can be obtained.

The Manufacture of Potassium Sulphate.—Potassium sulphate is generally made either from kainite or by acting on potassium chloride with sulphuric acid. Most of the potassium sulphate in the mines occurs in the form of kainite, which consists of potassium sulphate, magnesium sulphate and sodium chloride. The first step in preparing potassium sulphate is to manufacture an artificial schoenite by a system of re-crystallization. A cold saturated solution of kainite is employed for extracting fresh kainite. The solution is clarified, and on cooling deposits schoenite, *i.e.* potassium magnesium sulphate. Or mixtures of kainite and sylvinite are treated with a hot solution of kainite, when almost pure schoenite crystallizes out. This latter is very often used directly for agricultural purposes. When potassium sulphate is made from schoenite, a saturated solution of hot schoenite is run on to dry powdered potassium chloride, when the following reaction takes place :—

$$K_2SO_4.MgSO_4 + 3KCl = 2K_2SO_4 + KCl.MgCl_2$$

The potassium sulphate is separated from the liquor by centrifugal force, at a temperature of 40° C. (104° F.). Potassium sulphate made from schoenite is largely used for agricultural purposes.

Potassium Sulphate from Potassium Chloride and Sulphuric Acid.—This process is similar to the Leblanc soda process, p. 66, coarsegrained potassium chloride being employed. Sulphuric acid of a specific gravity of 1·67 is used for the reaction, and should, for purposes of economy, be made on the spot. It is unnecessary to use as strong an acid as in the Leblanc process, because the temperature of the action of potassium chloride is higher than that of sodium chloride. Sulphate of potash manufacturers prefer an open build of furnace, *i.e.* reverberatory, since a high temperature is required for decomposition. The ordinary decomposing pans are worn out in half the time they would serve for the Leblanc processes. The hydrochloric acid produced is saved, as in the Leblanc process. From a high grade potassium chloride of 98 % purity a potassium sulphate of 95 % purity can be made.

Potash Manure Salts.—There are many by-products in those industries where crude potash salts are produced. Fertilizers have been placed upon the market under the simple name of " Potash Manure Salts," blended up to some even figure of potash content, 20, 30 or 40 % ; these manures increased in popularity during the early years of the twentieth century. The constituents which enter chiefly into potash manure salts are natural sylvinite, kainite, muriate of potash or artificial carnallite and schoenite. On account of the different materials from which these potash manure salts are prepared, there is great variation in their colour and general appearance ; inspection is little guide to value. A typical sample of a 30 % potash salt contains about 48 % of potassium chloride, 27 % of sodium chloride. Sulphate of potash is the most difficult to produce, and, in consequence, the unit price of the potash in sulphate of potash is the highest ; whilst the miscellaneous potash manure salts are usually the cheapest per unit.

Sulphates *v.* Chlorides.—Excepting for the single case of the mangold crop, there are few occasions when chlorides are needed in any quantity as a manure. Further, as common salt is generally fed to cattle and horses, and all the sodium chloride fed to these animals passes into the manure heap, the ordinary dressings of well-kept farmyard manure contain no inconsiderable amount of common salt. So far as the British Isles are concerned, most districts are so little distant from the sea coast that sodium chloride, in the form of fine sea spray, is brought down by the rain in fair amounts. On the other hand, sulphur is an important element in the proteins. Sulphur, therefore, has a definite use for plants, whereas chlorine has not. Some particular crops, such as potatoes, are very adversely affected by any quantity of sodium chloride ; the harm appears to be due to the chlorine, and not to the sodium. There is, therefore, as a rule, a sound reason why sulphates are preferred to chlorides for manurial purposes. Looking back over the course of the use of potash salts for many years, most people have been struck by the fact that both the potash manure salts and kainite are becoming richer in chlorine and poorer in sulphate, and that there is a tendency for potassium chloride to be plentiful and potassium sulphate to be very scarce. As much potassium sulphate is made from potassium chloride by treatment with sulphuric acid, there is no reason why some of the cruder potash salts might not be treated in the same way. Whilst sodium and magnesium chlorides are frequently prejudicial to plants, the corresponding sulphates have an entirely different action. This point has been experimented on at Rothamsted on wheat for about 70 years. As a result it has been found that sulphate of potash, although very beneficial indeed, is not so much ahead of sodium sulphate or magnesium sulphate as to justify any very much greater price for potassium than for sodium and magnesium. Whilst the addition of sulphate of potash has added 8 bushels of dressed grain, the addition of sulphate of soda has added over 6 bushels, and the addition of sulphate of magnesia just under 6 bushels, but when all those substances are added, there

was one bushel more than when sulphate of potash alone was used, so that it is clear that the sulphates of soda and magnesia are really beneficial, whether potash is supplied or not. For the purpose of converting the potassium minerals into useful fertilizers for crops, it is a mistaken process to attempt to prepare a pure potash salt, and it is a far greater mistake to leave chlorine in if it can be avoided. It would therefore be very much better to treat crude potash salts with sulphuric acid and obtain the sulphates than to attempt the removal of the sodium and magnesium. The sodium and magnesium are useful; it is the chlorine that is objectionable. On p. 134, when dealing with the superphosphate industry, the problem of the consumption of sulphuric acid in the future has been discussed. There is a possibility that there may be too much sulphuric acid, and it is necessary to find some useful purpose to which this surplus acid can be put. The treatment of crude potash salts with sulphuric acid is certainly one valuable way of disposing of surplus sulphuric acid. No plant beyond that used in the Leblanc process is necessary; sulphuric acid is generally made on the spot at those works; the hydrochloric acid produced would be absorbed by exactly the same plant that is already there, and the only difference would be that the resulting salt cake would be sold directly for fertilizer purposes, instead of being subsequently worked up for sodium carbonate and the recovery of sulphuric acid.

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Section V.—BONE MANURES

Bones.—So far as their origin is concerned, bones have been described on p. 72. Previous to being degreased, bones are of little value for fertilizing purposes. After bone fat has been removed, bones can be ground up to various degrees of fineness. Bones that have had the grease removed, but are still rich in nitrogenous organic matter, are tough and difficult to grind, and are generally put upon the market as a coarse meal. Those qualities of bone which have not merely been degreased, but have been also partly deprived of their gelatinous material, contain far less fibrous organic matter, are somewhat porous, and grind easily to a very fine powder. There are about three different sorts of bone meal and bone dust to be found on the market. The best quality bones, after having their grease removed, contain about 5 % of nitrogen, equal to a little over 30 % of gelatinous matter, 45 % of calcium phosphates and 15 % of water, the residue being a little calcium carbonate and small traces of other compounds, amounting on the whole to 5 or 7 %. The lower qualities of bone meal, obtained from bones containing higher proportions of calcium phosphate and lower proportions of organic matter, may often be met with containing about 4 % of nitrogen and 45–50 % of tri-calcium phosphate. Steamed bone flour may contain anything from 1 to 3 % of nitrogen, and from 50 to 60 % of tri-calcium phosphate, some of the finest bone flours containing about 1½–2 % of nitrogen and 55 % of tri-calcium phosphate. The use of bones containing 30 % gelatinous matter as manure is a wasteful process; bones containing the lower proportions of nitrogenous matter decompose rapidly in the soil and are therefore to be preferred. Gassmann considers that the phosphate in bones is a carbonic apatite, $Ca_{10}(PO_4)_6.CO_3$ (see p. 120).

Dissolved Bones, Vitriolized Bones.—Bones have been treated with sulphuric acid for many years as a means of obtaining the phosphates in a more soluble form. Some, at least, of the difficulties of solubility have been also overcome in recent years by superior methods of grinding, but when treatment with sulphuric acid was at first commenced dissolved bones had only to compete with raw bones, containing grease and only coarsely ground. There was, therefore, a much greater difference between the dissolved bones and undissolved bones of 50 years ago than there is in those fertilizers to-day. The manufacture of dissolved bones is very similar to that of mineral superphosphates. Bones, which should be degreased and finely crushed, are reduced to powder by means of a steel ball mill and passed through a 50-mesh sieve. The bone dust is then mixed with the desired amount of sulphuric acid. Much variation in method takes place in different works, owing to the difficulties of treating bone meal and sulphuric acid. In some works a sulphuric acid rather stronger than that used for superphosphate is employed; such a mixture heats quickly, and reaction takes place at a rapid rate; there is some slight risk of browning the bones by means of the burning property of sulphuric acid. Owing to the rapidity of the action, the mixing must take place quickly, and the mixture should be transferred to the den without loss of time. Some manufacturers, puzzled by the difficulties of quick mixing and quick charging, prefer to use a much more dilute acid, which, whilst it acts less rapidly, produces a very damp and unsatisfactory dissolved bone. Bones contain far less fluorine and chlorine than do most of the rock phosphates, but some objectionable gases are given off in the manufacture of dissolved bones; therefore the same precautions are necessary to prevent the workmen being exposed to obnoxious and possibly poisonous fumes. Less carbonic acid is evolved when dissolving bones than when dissolving rock phosphates, hence the mixture does not froth up to a bread-like consistency in the same manner as it does in making superphosphate. Where the manufacturer has been successful in using a fairly strong acid with quick

mixing and charging, a good dissolved bone can be removed from the den; by putting it into heaps and occasionally spreading, a very satisfactory dry dissolved bone can be made. Where manufacturers use a weak acid the excess of the water must be driven off, and therefore artificial drying in some way is necessary. Artificial drying ovens with the necessary air ventilation can be obtained, but quite a satisfactory result may be produced by spreading the dissolved bone on a stone floor, heated by flues, and turning it over from time to time. The process of dusting with bone meal, or, better still, steamed bone flour, may be practised in the same way as in the dusting of superphosphate with mineral phosphate powder, p. 150. By such methods of drying and dusting, the correct dry condition can be obtained that is so necessary for sowing on the field with manure distributors. The difficulty of obtaining a dissolved bone in a fine dry condition is so great, that it is never desirable to make any effort to push the solution as far as it is pushed in the manufacture of mineral superphosphates; frequently only half the total amount of phosphate present is rendered soluble, and a typical good class dissolved bone should contain 3% of nitrogen and 15% of phosphates rendered soluble, with 15% of phosphates remaining insoluble. Great variations occur in the composition of dissolved bone, since the bones from which it is made themselves vary, the method of manufacture varies, and the degree to which solution is attempted is also very variable. In some cases manufacturers produce a dissolved bone with more than three-quarters of the total phosphates in a soluble condition; in this case the remarks which are made on p. 144 with reference to the relationships between free phosphoric acid and tri-calcium phosphate will very nearly apply. In other cases, where only half of the phosphates are dissolved, these relationships are no longer true, since the tri-calcium phosphate was not originally completely converted into mono-calcium phosphate, but remained from the beginning to a large extent in the form of di-calcium phosphate.

The sulphuric acid used produces a marked chemical

change in the gelatinous matter of the bone; the nitrogenous organic matter is partly peptonized and some amino acids and ammonium sulphate is formed.

Nitrogen in dissolved bone occurs in the forms of humic nitrogen, glycine, leucine, alanine, argenine, lysine, histidine, ammonia and unaltered protein. (See Table 20.)

TABLE 20.

FORMS OF NITROGEN IN DISSOLVED BONES.

Ammoniacal nitrogen	0·03–0·08 per cent.
Humic nitrogen	0·04–0·11 ,,
Basic nitrogen (argenine, lysine and histidine)	0·11–0·31 ,,
Amino nitrogen (glycine, leucine and alanine) ..	0·38–1·12 ,,
Protein nitrogen	0·18–0·48 ,,
Total nitrogen	0·78–2·10 ,,

The sticky and almost gummy consistency of damp dissolved bones is brought about by the presence of free phosphoric acid and amino acids.

Bone Compound Manures.—Bones are often compounded with other manures, such as superphosphate. The manufacture of dissolved bones presents many difficulties which add considerably to the expense, with little advantage from the fertilizing point of view. When sulphuric acid acts upon bones, it not merely dissolves the phosphate, but it also dissolves the organic nitrogenous material, hence dissolved bones contain tri-calcium phosphate, di-calcium phosphate and mono-calcium phosphate, which behave differently in the soil as regards their rates of availability. The nitrogenous matter is also somewhat broken up, a little ammonium sulphate is produced, some of the nitrogen is converted into amides, amino acids or other soluble nitrogenous matter, though a part remains un-acted upon by the sulphuric acid. There are consequently several forms of nitrogen and phosphates present in dissolved bones; this mixture is undoubtedly of very considerable practical value when used as a fertilizer. However accurately the farmer may judge the need of his soil and crop, in no case can he possibly foresee the weather for months ahead, and therefore

a large portion of his calculations must be left to chance. The maximum utilization of any fertilizing ingredient can only take place when everything is favourable. Hence it may happen that the greatest need of a fertilizing material will occur in one case during the early stages of growth of the plant, on another occasion during the main period of plant growth, while the critical point in the history of a third plant may be its ripening period. For the purpose of promoting germination of a seed, readily soluble constituents are absolutely essential. Very considerable acceleration in the rate of germination of seed can be produced by very weak solutions of various salts. Highly soluble materials are therefore very efficacious at that period of growth. For later periods of growth, root stimulation is desirable, and roots do best if they have to travel some little distance to find their food; the encouragement of a mat of roots close to the stem is undesirable, and likely to produce serious difficulty should drought intervene. There is consequently a great advantage in having fertilizing ingredients in several different forms in the fertilizing mixture used, but to obtain that end by treating bones with sulphuric acid is an unnecessarily expensive process. The same results can be obtained much more economically by mixing superphosphate, bone meal, perhaps a little rock phosphate, sulphate of ammonia and other ingredients. Steamed bone flour is a particularly convenient article for making a mixture, since it dries up the superphosphate with which it is mixed. As described in the article on Superphosphate (p. 151), there are difficulties in making a dry superphosphate, even under the best conditions; the power to be able to add a really useful drying material like steamed bone flour is very valuable. Superphosphates which are difficult to obtain in a dry condition may even be hurried through the den, and then subsequently dried by admixture with bone meal. This method provides an economical system of obtaining a bone compound containing at least two kinds of phosphate and one kind of nitrogen. The composition of any such bone compound is just exactly what the manufacturer desires,

since bone meal can be added to superphosphate to any extent that may be needed.

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Section VI.—COMPOUND MANURES

Ammoniated Superphosphate.—This very useful compound manure is obtained by mixing the requisite quantities of superphosphate and sulphate of ammonia. To make a mixture containing 1 % of nitrogen, 19 cwt. of superphosphate and 1 cwt. of sulphate of ammonia should be used. Mixtures containing 7 % of nitrogen, made from 13 cwt. of superphosphate and 7 cwt. of sulphate of ammonia, are occasionally used, but only for very special purposes. The superphosphate is weighed out according to the calculated amount, placed in a heap, and levelled, the sulphate of ammonia is also weighed out, placed on the top of the superphosphate heap and levelled. A man now digs vertically down into the heap and transfers this mixture to a barrow, which is wheeled away and worked through a ½-in. screen. When it is all passed through, the screen is exchanged for a ¼-in. screen, and passed back again. By digging vertically, so as to obtain a fair sample from top to bottom at all stages of the process, the mixing becomes very complete. Special machines, "batch mixers," "pulver blenders," or "pulvo mixers," can now be obtained to save much of the labour involved. The superphosphate and sulphate of ammonia should be weighed out as before, but can be wheeled straight away to the cups of an elevator which delivers the mixture to the hopper on top of the pulvo mixer. On falling into the pulvo mixer, revolving arms blend the material and throw it against screens, through which the fine material passes, to be promptly bagged at the spout of the pulvo mixer.

Sulphate of ammonia checks the retrogression of superphosphate (p. 154). Should such a mixture show any slight tendency to cake, it can be easily broken by passing through a screen. As a rule any such tendency to cake is

only produced at the first stages of mixing ; once mixed and screened, there is little risk of a second caking (see p. 12).

The general experience in the past of occasional difficulties with the manufacture of ammoniated superphosphate, owing to its tendency to cake, is connected very largely with the small relative amounts of other forms of nitrogenous matter that are used in these mixtures. During recent years, however, the scarcity of organic nitrogenous fertilizers, and the Government controlled low price of ammonium sulphate, have made ammonium sulphate the most easily obtainable form of nitrogen, and other forms of nitrogen have dropped out of use. The presence of comparatively large quantities of ammonium sulphate in admixture with superphosphate in the absence of other materials has produced an extra tendency to "set." The setting frequently takes place so slowly, that a compound fertilizer may appear, when placed in bags at the factory, to be in a fit condition for sowing on the land, but, after storage or transit it is found to have set into hard lumps, which may necessitate cutting away the bags. When the manufacturer has much space at his disposal and can manufacture in advance, the difficulty of setting disappears, because he stores the fertilizer until it has finished setting, and then regrinds it before dispatch, but recent pressure of trade has often rendered this precaution impracticable. Experiments that have been conducted to determine the conditions under which superphosphate and ammonium sulphate undergo the process of setting, show that mixtures containing 5–6 % of ammonia give the greatest trouble. Much depends, however, upon the amount of moisture in the ammonium sulphate that is used for mixing, samples containing 4 % of water setting much more rapidly than those containing only 1–2 %. A difficulty occurs where setting only takes place to a slight extent; the mixtures are left damp. When sulphate of ammonia containing 3–4 % of water is used, the mixtures set rapidly, appear lighter in colour, feel dry and gritty, and can be easily reground. Further trials to discover whether the addition of ground Gafsa phosphate produces much influence on the

result, show that after standing a week with slight pressure, the mixtures are much drier than when no rock phosphate is used. The influence of water is very noticeable, the damper the sulphate of ammonia the quicker does the setting take place, whether rock phosphates have been added or not. Whilst moisture tends to increase the rapidity of setting, the increase is much more marked when the free acid of the superphosphate is reduced to a low figure. If it is desirable to hasten the completion of setting in any of these mixtures, it is necessary to use sulphate of ammonia which contains 3–4 % of water, instead of using a very dry sulphate. When rock phosphate, superphosphate and sulphate of ammonia are mixed, the whiteness, dryness and hardness increases with the amount of rock phosphate employed. Compound fertilizers set rapidly if made with about 5 % of ground rock phosphate and about 20 % of sulphate of ammonia containing 3–4 % of water; after eighteen days' rest and regrinding, further setting need not be feared. As explained on p. 187, there is no agricultural necessity for compounding fertilizers containing nearly all their phosphoric acid in soluble form; the field results are often as good with lower proportions of soluble phosphates, provided that the insoluble phosphates are in a very fine state of division.

If for any reason whatsoever it is desirable to retard the setting of mixtures of sulphate of ammonia and superphosphate, a larger amount of free acid may be present, and therefore both the superphosphate and the sulphate of ammonia should be more acid than is commonly considered suitable. It will, however, be very difficult to make such a mixture in the form of a dry, fine powder. A fertilizer which has not been allowed to set is moist and sometimes sticky, whereas one which has set and has been ground again is very dry, and altogether in a far better condition for use on the field. So long as the present abnormal state of trade prevails, good condition will have little monetary value; when business becomes less congested and more normal, there is little doubt that the farmer will, as before, attach much importance to condition in these mixtures. The

manufacturer will then have to decide whether it is best to attempt to prevent setting or to hasten setting and get it done with. In the former case, he will use acid but dry ingredients; in the latter case, he will use neutral and damp ingredients, allowing them to stand in store for a period of two to three weeks, and regrinding and passing them through a fine sieve before bagging.

Sulphate of ammonia tends to dry up the superphosphate, should it be slightly damp, because of the formation of a double compound of calcium sulphate and ammonium sulphate. If in mixing any of the above compounds, a superphosphate of about 30 % be used, then the compound manure produced will vary from 28 % phosphates and 1 % nitrogen to 20 % phosphates and 7 % nitrogen in the extreme cases quoted on p. 179. As a rule, lower proportions of soluble phosphates are required, hence either a larger amount of insoluble phosphate is used, or a certain amount of gypsum may be employed, to reduce the percentage of soluble phosphates in the compound. There is a distinct advantage in having two kinds of phosphates, hence a quantity of rock phosphates may be employed for this purpose. Where a superphosphate is mixed with rock phosphate, it is desirable that the rock phosphate selected is one that will give a minimum reversion. In Table 21, p. 183, Robertson gives the result of using a Gafsa rock phosphate, mixed with superphosphate in equal amounts, to measure the degree of reversion.

According to his experiments, "Gafsa rock phosphate (a North African phosphate) is probably the most suitable for mixing purposes, as it very rarely contains more than 0·75 % of calcium oxide in the form of free carbonate. This phosphate has the additional but doubtful advantage of being more soluble in 2 % citric acid than any of the other rock phosphates. Egyptian phosphate is probably the next best for mixing purposes, and then come Florida pebble phosphate, and the Makatea Island phosphate, followed by Tunisian and Algerian phosphates.

"If Gafsa phosphate containing at least 26 % of

phosphoric acid is used for mixing with superphosphate, the reversion of water-soluble phosphate will be small. But if low grade varieties of rock phosphate, containing 25 % and under of phosphoric acid, are used, the reversion of the water-soluble phosphate to the water-insoluble form in the superphosphate mixture will be considerable. Superphosphate and rock phosphate produce a very nice mixture, particularly if the superphosphate is in a friable condition.

TABLE 21.

GAFSA ROCK PHOSPHATE AND SUPERPHOSPHATE.

	Immediately after mixing.	Oct. 20, 19 hours.	Oct. 23, 96 hours.	Nov. 3, 14 days.	Nov. 23, 35 days.	Jan. 3, 76 days.	Feb. 13, 117 days.	May 15, 208 days.	Theoretical composition of mixture.
Water-soluble phosphoric acid ..	% 5·82	% 5·03	% 4·72	% 4·76	% 4·53	% 4·27	% 4·30	% 4·42	% 5·95
Water-soluble phosphate	12·70	10·98	10·30	10·39	9·89	9·32	9·39	9·65	12·99
Citric-soluble phosphoric acid ..	11·35	12·08	11·90	11·80	11·75	11·86	11·53	12·09	11·16
Citric-soluble phosphate	24·78	26·37	25·98	25·76	25·65	25·89	25·15	26·39	24·35
Citric-soluble lime ..	18·26	18·02	18·10	18·00	18·02	18·18	17·90	18·19	15·86
Total phosphate ..	—	—	—	—	—	—	—	—	41·89
Citric solubility of phosphate ..	58·9	62·5	62·0	61·5	61·2	61·8	60·0	63·0	58·1

" Mixtures of rock phosphate and superphosphate might be rendered even more efficient if the rock phosphate was ground a great deal finer than it is. As a rule rock phosphate for the making of superphosphate is not ground quite so finely as basic slag. From 70 to 80 % only passes a sieve with 10,000 holes to the square inch, whereas basic slag has a corresponding fineness of from 80 to 90 %. It is perfectly feasible to have the rock phosphates ground so that upwards of 80 % will pass a sieve with 40,000 holes to the square inch, and there is every reason to suppose that by so doing the efficiency of the mixture with superphosphate would be greatly improved."

It will be noted that in the quantities which Robertson used the amount of water-soluble phosphoric acid is reduced

very seriously, but for the purpose of manufacturing ammoniated superphosphate that amount of rock phosphate need not be used. It would not be desirable to have more than two-thirds of the total amount of phosphate in an insoluble form. 12 cwt. of superphosphate, 5 cwt. of Gafsa rock phosphate and 3 cwt. of sulphate of ammonia would make a convenient mixture for many purposes, giving about 14 % of soluble phosphates, 24 % of insoluble phosphates and 3 % of nitrogen.

Potassic Superphosphate.—Superphosphate may be mixed with any potash manure or potash manure salts; these latter have, in the past, usually proved to be the cheapest. Blast furnace dust is too weak for general compounding; wood ashes contain too little potash and too much carbonate. If the potash manure employed contains much chloride, there is some tendency for the manure to become damp on long standing, but as a rule most of the potash manures help to dry the superphosphate and check retrogression. A very common practice in the past has been to use a potash manure salt containing about 30 % of potash. By using 1 cwt. of such a potash manure salt and 19 cwt. of superphosphate, a manure containing 1½ % of potash will be produced; with 5 cwt. of potash manure salt and 15 cwt. of superphosphate, a compound fertilizer containing 7½ % of potash manure would be produced; these quantities represent about the limits of ordinary practice. Potassic superphosphate is suitable for grass land on the lighter soils, and on tilled land where nitrogenous constituents are best applied as a top dressing. For mangolds a convenient application would be 12–15 tons of dung, 5 cwt. of potassic superphosphate containing about 29–39 % of soluble phosphate, and 7 % of potash, leaving the salt and nitrate of soda, say 5 cwt. of the former and 2 cwt. of the latter, to be applied as top dressings in two or three fractions. One reason for such a distribution is that neither the potash nor the phosphate is liable to be washed out of the soil, and both may be applied early; a second reason is that soluble mineral materials of this kind are required during the germination

of the seeds. The top dressings of sodium chloride and nitrate of soda easily wash out of the soil, and are mostly required at periods in the life of the plant between germination and flowering; but flowering is not reached in the mangold crop. The late application of these ingredients permits the farmer to reduce the risk of "bolting" in mangolds, an advantage which would be lost if all the ingredients were applied before sowing the seed.

Complete Manures.—Occasionally manures of a complete character are required. The operation of compounding complete manures presents no special difficulties beyond those alluded to in describing the manufacture of ammoniated superphosphate and potassic superphosphate. For making these compounds some kind of mixing machine is needed; either a revolving wheel with several pegs, or a disintegrator, or a pulvo mixer (see pp. 116, 179). Care must be taken that rock phosphates, or other material containing calcium carbonate, must only be used sparingly, to avoid the excessive reversion of superphosphate, unless a large proportion of insoluble phosphate is asked for. When several ingredients are mixed, the advantage of various forms and degrees of solubility can readily be obtained. The most important materials for compounding are superphosphate, bone flour, sulphate of ammonia, potash salts and rape dust, all of which can be blended together very satisfactorily. Rape dust is very useful in checking "setting" in a compound manure (see p. 180); very fine, dry materials, which do not clog any type of machine, can be made in this way. It is better to leave nitrate of soda out altogether, but both salt and gypsum may be used in mixtures if needed.

It is quite clear that on certain types of soil the advantage of superphosphate has been somewhat exaggerated. A considerable portion of the phosphates may be of a far less soluble form without any disadvantage at all. This fact is very well illustrated by Hendrick, who collected the average of 66 field experiments carried out during the years 1911–14 throughout several of the northern counties of Scotland. The most important of these results are represented in

Table 22, p. 187. In the experiments recorded in the Table, manure was applied equally on all plots at the rate of about 12 tons per acre. Sulphate of ammonia and 30 % potash manure salts were applied equally to all plots except No. 1, at the rate of ½ cwt. per acre. An equal amount of phosphoric acid, approximating 50 pounds of P_2O_5 per acre, was given to each of the plots excepting plot No. 1. From plots 8–11 one-third of the phosphoric acid only was obtained from superphosphate, whilst two-thirds were obtained from one of the other phosphatic manures, which were in all cases of a very much lower order of solubility than superphosphate. As is to be expected in field experiments, the individual trials showed great variation. In some cases this was due to the fact that the soil was already in such a high condition that a full crop was obtained without the use of artificial manure, whilst in other cases the entire absence of artificial manure resulted in hardly any crop at all. It is important to recognize that for a real trial of the relative value of soluble and insoluble phosphates, the experiments should have been conducted throughout an entire rotation, which adds much to the difficulties of experimental trials. It should be noted that the present test of only one crop in the rotation would be unfairly disadvantageous to the insoluble manures. It may be taken for granted that if there is any difference between a soluble and an insoluble fertilizer, the soluble fertilizer will produce its best results in the first year, and, therefore, one may safely assume that the results for the whole rotation would have been more in favour of the insoluble phosphates than the experiments on one crop in the rotation were. The general result of the experiments is to show that the average benefit of superphosphate is only slightly greater than that of insoluble phosphates. It will be noted that the amount of phosphate is by no means extravagant; it would therefore be wrong to assume that the reason, why the insoluble phosphates appear to be as good as the soluble ones, was that one-third of the dressing of phosphates was sufficient. The only conclusion one can draw from these experiments is that soluble phosphate is some-

times overrated, and that on many fields a portion of the phosphates in a compound manure might safely be in an insoluble form. It is essential that insoluble manures be finely ground.

Compound manures, if produced at definite compositions, fill a useful part in the agricultural industry, but too much attention should not be paid to mere names applied to them. It is not practicable to specify any particular mixture as being specially suited to one or another crop under all conditions. A useful manure for the hay crop of a four-course rotation is given on p. 204. Such a fertilizer might be made by mixing 12 cwt. superphosphate (30 %) with 3 cwt. sulphate of ammonia, 1 cwt. steamed bone flour and 4 cwt. potash manure salts (30 %), and should be used as explained on the page quoted.

TABLE 22.

FIELD EXPERIMENTS WITH PHOSPHATES UPON TURNIPS, 1911–14.

Average of 66 experiments.

Plot.	Tons.	Cwts.
1. No artificial manure	13	17
2. Sulphate of ammonia, potash manure salts, and superphosphates	20	12
3. Sulphate of ammonia, potash manure salts, and basic slag	20	0
4. Sulphate of ammonia, potash manure salts, and ground mineral phosphate	19	10
5. Sulphate of ammonia, potash manure salts, and steamed bone flour	20	7
6. Sulphate of ammonia, potash manure salts, and bone meal	19	11
7. Sulphate of ammonia, potash manure salts, and dissolved bones	20	3
8. Sulphate of ammonia, potash manure salts, and mixture of superphosphate and basic slag	20	15
9. Sulphate of ammonia, potash manure salts, and mixture of superphosphate and ground mineral phosphate	20	8
10. Sulphate of ammonia, potash manure salts, and mixture of superphosphate and steamed bone flour	20	15
11. Sulphate of ammonia, potash manure salts, and mixture of superphosphate and bone meal	20	11

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PART IV.—THE TRADE IN FERTILIZERS

SECTION I.—THE VALUATION OF FERTILIZERS

FOR very many years past it has been the habit to value fertilizers according to the unit value system, in which it is assumed that the value of the fertilizer is strictly in proportion to the percentage of the important ingredients present. Such a system by no means takes into account all the factors concerned. From the manufacturer's point of view, fertilizers cannot be produced by such a system, since the costs of manufacture do not follow such rules. From the farmer's point of view, the increased crop obtained does, more or less, correspond with the increased percentage, since in practice he would use such materials as were necessary to provide him with a certain quantity of fertilizing ingredients. It is not quite correct to say that fertilizing value is proportionate to the percentage of fertilizing ingredient, since increasing quantities of fertilizing material do not produce equivalent quantities of crop increase. If a very small amount of any fertilizing ingredient is added to the soil, the effect is frequently very slight. It is with increasing amounts that rapid increase in crop production follows, but ultimately a limiting value is approached, and further additions of fertilizing materials will produce no corresponding increase in crop, a condition of affairs which is commonly explained by "the law of diminishing returns." If increasing quantities of fertilizing material are still added to the soil, injury may be done, and the crop returns become even less. In practice the farmer tends to use rather less fertilizer than is capable of producing the most economical results, and therefore at the stage of development which is commonly reached in the

application of fertilizers, the percentage composition of the fertilizer varies almost proportionately to the crop yields.

From the farmer's point of view there is another consideration which is very important, although frequently lost sight of. The farmer cannot bring on to his land any fertilizer without spending money upon distribution on the land, cartage from the station and railway freight. Some portions of the last item may be hidden away in the manure manufacturer's bills. From the farmer's point of view, therefore, a manure having a very low percentage of essential ingredients is worth rather less than nothing, since it will cost him more to put it on to the land than he will receive from the increased crop production. Such a case is rare in practice, because almost any material put upon a soil will produce some physical improvement and therefore the minus value need not be regarded very seriously. Recently the Fertilizer Prices Orders of 1917 and 1918 have put a somewhat different complexion upon the system of valuation. Murray, Smetham and several other writers have drawn attention to this point of view.

Value of Sulphate of Ammonia.—According to the Fertilizer Prices Orders of 1918, sulphate of ammonia is valued according to the percentage of ammonia, rising in stages, each ¼ % of ammonia being worth 3*s.* 3*d.*, that is to say, 1 % of ammonia is charged 13*s.* The standard sulphate of ammonia, containing 24½ % of ammonia, is therefore worth £15 18*s.* 6*d.* The price charged during June, July and August, 1918, was £15 5*s.*, whereas the price charged for March, April and May, 1919, was £16 15*s.* There is left a minus 13*s.* 6*d.* or a plus 17*s.* 6*d.* for the zero price, that is to say, for the theoretical value of sulphate of ammonia which contains no ammonia at all. The variation in price according to season is placed entirely upon this zero price, and not upon the unit price of 13*s.* per unit of ammonia. It is obvious that this is quite illogical, since the variation in the season price is a matter which concerns the farmer, and not the producer. The zero price should be a price between the maker's cost of production of

sulphate of ammonia, and the cost which the farmer would have to incur in applying sulphate of ammonia to the land, apart altogether from any value it may possess to the farmer, whilst any seasonal variations in price are matters which concern the farmer alone, who should pay for them.

If the prices of sulphate of ammonia are plotted on squared paper, it is clear that the curve in this case is a straight line, and therefore follows the formula $V = a + bp$, where V represents the value, a the zero price, b the unit price and p the actual percentage, that is to say, in such a formula a is minus 13½ to plus 17½, according to season, and $b = 13s$. If we attempt to represent the matter from the maker's point of view, a should be a much higher figure, perhaps even £5, whilst b would have no particular value at all, since the cost of making sulphate of ammonia of high grade is not much greater than that of making it of low grade. From the farmer's point of view a ought to be a minus figure; probably minus £1 5*s*. would be a fair allowance to cover cost of application, cartage from the railway station and some share of the railway freight, but b might be a very high figure indeed. It might be argued that the zero price, from the farmer's point of view, should be even lower, since the sulphuric acid in sulphate of ammonia is of little use, and may even be harmful. About 10*s*. worth of lime is removed from the soil by a ton of sulphate of ammonia. The zero price might, therefore, be put at minus £1 15*s*. Something like £1 12*s*. would be the profit of the crop obtained by the farmer for the value of the factor b in the formula. There is, consequently, a very wide range of opinion as to what would constitute the value of any article when the seller and the buyer have such totally different points of view. The values adopted by the framers of the Prices Orders clearly come easily between these extreme points of view, but it certainly seems as if the framers' assumptions were based too low for the factor a, *i.e.* the zero price, and it would clearly be much fairer if the zero price were raised, say to allow a to equal 20*s*.

and b to vary according to season from about 12*s.* to 13*s.* If simplicity of calculation is considered a point of great necessity, it would be better to give the ¼ % of ammonia an even number of shillings, say 3*s.*, since the error of ¼ % is actually allowed in the guaranteed analysis; this system would allow the zero price a to fluctuate from 11*s.* to £2 1*s.*, according to season. It will be seen, therefore, that even in such a simple case as the question of sulphate of ammonia, the calculation of values is far more complicated than has usually been allowed for in the text-books.

The orders for 1919–20 for sulphate of ammonia give a zero price of minus £1 12*s.* a ton, and a unit price for ammonia of 16*s.*, which is equal to a unit price for nitrogen of 19*s.* 5*d.* In other words, the interests of the farmer are here predominant, and the point of view of the producer is not considered.

Nitrate of Soda.—The Board of Agriculture recently (May, 1919) fixed the price of nitrate of soda at £10 a ton, corresponding to £1 5*s.* for 1 % of nitrogen, as against rather under 16*s.* for 1 % of nitrogen in sulphate of ammonia. Mr. Kellaway stated in the House of Commons that there is at present no appreciable demand for nitrate of soda from farmers in this country. At such an increased price over sulphate of ammonia, it would not be worth the farmer's while to purchase nitrate of soda.

Ammonium nitrate has been offered by the Board of Agriculture (March, 1919) at £25 a ton for about 33⅓ % nitrogen. This is equal to 15*s.* per unit of nitrogen, or much below the unit price of nitrogen in sulphate of ammonia.

The Valuation of Basic Slag.—Similar statistical treatment enables one to draw a curve of the prices charged in the case of basic slag. In treating any unknown curve, one can attempt to solve it by a formula of the form of $V = a + bp + cp^2$, etc., where the meanings of the symbols are the same as before, with the addition that c is a new constant. If this equation is solved for the basic slag prices, we find that $a = 47s.$, $b = 78s.$ and $c = 0{\cdot}0174s.$

If we take the simpler view of assuming the curve to be almost a straight line, and adopt the formula $V = a + bp$, a works out at £2 3*s.* 4*d.* The error allowed for in the case of basic slag is as much as 2 % in the analysis, corresponding to 2*s.* 8*d.* The assumption that the price fits a straight line only causes a maximum error of 1*s.* 9*d.* which is easily within the allowed limit. There is, with basic slag, no justification in departing from the simpler straight line, and the table might be made simpler without error.

It will be noted that in the case of basic slag, however one may calculate the figures, the large zero price of over £2 per ton is allowed in contradistinction to sulphate of ammonia, which seems to have been allowed only a minus zero price. On consideration of the conditions under which these articles are manufactured, it will be noted that there is a striking difference between the position of the two manufactures. The manufacturer of basic slag may dump all his material in a heap, at a very small cost; therefore, the whole cost of breaking, grinding, sieving, bagging, etc., must be paid by the farmer, who pays a high zero price. On the other hand, the sulphate of ammonia manufacturer is not at liberty to run his waste ammonia liquors into the nearest stream; it would cost him, in any case, something to dispose of his ammonia liquors, even if there was absolutely no market for it. There is, therefore, a reason why the zero price of sulphate of ammonia should be lower than that of basic slag.

The values which have been officially placed upon the handling of manures are given under the head of compound fertilizers, and have been readjusted by Smetham where cost of mixing, bagging, distributing and transfer is assigned by him to be worth about £2 7*s.* 6*d.* per ton. Assuming that the cost of grinding the slag and the cost of mixing compound manures is not likely to be very seriously dissimilar, £2 7*s.* 6*d.* is probably a fair estimate of the zero price, which agrees very well with the figures deduced from the curve. It makes little difference to the manufacturer whether the slag is of high or low grade percentage of phosphate; as

the costs of handling and grinding do not vary according to the percentage of phosphate, but according to the percentage of iron which occurs as metal.

The farmer's values may be deduced from the experiments which have been conducted on the use of basic slag. Some of the oldest and best known of these have been conducted at Cockle Park, and are described in Gilchrist's reports in the Cockle Park Guide for 1918, which show that the actual profits to the farmer are something like £1 15*s.* per ton for each 1 % of phosphate. Cockle Park is, however, particularly suited to basic slag, and it would be more reasonable to assume that the average profit of slag in the country is considerably less. One might also safely assume that the cost of cartage, etc., would be somewhat as before, say £1 5*s.* per ton, hence the equation $V = a + bp$, if made to represent the farmer's profits from the use of basic slag, would be solved by a = about minus £1 5*s.*, and b = about 17*s.* On the other hand, the amount of lime in basic slag would give a plus zero value of about 4*s.* a ton, reducing the value of a to minus 21*s.* It will be seen that a compromise has been effected in the Orders between the discordant points of view of the producer and the consumer of basic slag. It would be better for the manufacturer to work with a zero value much lower than that which has been assigned.

The new orders for 1919–20 do not modify the prices for basic slag sufficiently to alter the deductions drawn from the 1918 orders.

The Value of Superphosphate. — Superphosphate presents a different case to that of basic slag and sulphate of ammonia. Superphosphate is not a by-product, it is a specially manufactured article. It may be true that sulphuric acid might become a waste product of zinc smelting, but that day is not here yet, and in any case rock phosphate must be imported and paid for by the manufacturer of superphosphate. The process, moreover, is somewhat expensive, hence a higher zero point should be looked for. The manufacturer of superphosphate buys his rock phosphate on a unit

price basis, and cannot part with his finished superphosphate excepting on terms which recognize both a zero point and a unit value. The cost of manufacture is not quite the same with different grades of phosphate, the higher grades of superphosphate being more difficult to prepare than the lower grades. The profits from the use of superphosphate are of about the same magnitude as those obtained from basic slag, the substitution of one manure for the other being largely a question of soil and crop. On the whole, the value of crops usually grown with the aid of superphosphate is higher than the value of crops grown by basic slag.

If we plot a curve for the price of superphosphate, in the hope that the straight line curve will fit sufficiently well, we find that this assumption will not serve as it did with basic slag. If we make the effort to solve the equation $V = a + bp$, the value of a becomes about 30*s.*, and the value of b becomes 3*s.* 3*d.* The curve conforms very badly, and the error of the curve frequently exceeds the error allowed for analytical variations. If we proceed a step further, and attempt to solve the problem by the equation $V = a + bp + cp^2$, b becomes so small that it can be omitted, and the equation reduces to $V = a + cp^2$, which is evaluated as $a = 82$ shillings and $c = \cdot 055$ shilling. Here the solution $a = 82 + \cdot 055\, p^2$ conforms to actual values within a few pence of the schedule. As the allowance for error in superphosphate analysis is 1 %, equal to about 3*s.*, the fit of the curve to the equation $V = a + cp^2$ is sufficiently close. It is clear, therefore, that in the case of superphosphate, the principles underlying valuation are different to those which determine the values of basic slag and sulphate of ammonia. Although the theoretical problem in the schedule appears to be very complicated, it works out very simply in practice, as shown above. It will be noticed that the zero price for superphosphate by this formula works out at over £4, but that is perfectly reasonable, considering the cost of manufacture. It is clearly, therefore, not in the interest of the farmer to purchase low grade superphosphate, since he has to pay such a high price before he receives

anything of value. The orders for 1919–20 for superphosphate prices suggest higher values.

The Valuation of Compound Manures.—The framers of the schedule have introduced under the head of compound manures a slightly different method of arriving at their results. The value of the nitrogen is placed at 18*s.* 6*d.* per unit, which is equivalent to 15*s.* 3*d.* for ammonia, instead of 13*s.*, as in sulphate of ammonia. Soluble phosphates are allowed for at the uniform rate of 4*s.* 3*d.*, whilst citric soluble phosphates are allowed 2*s.* 6*d.* per unit, insoluble phosphates 1*s.* 6*d.* per unit, and potash is put at the high value of £1 5*s.* per unit. The price in May, 1919, for mixing, bagging, distributing and average transport worked out at £2 15*s.* per ton, although discounts are allowed for early deliveries. Hence the zero point is £2 15*s.*, but the curve is a straight line. It does not seem a very logical system to pay a higher unit price for valuable ingredients in a compound manure than for those in other fertilizers, but it is not altogether to the advantage of the farmer to consider it from this point of view. Nitrogen in mixed forms is more certain in its benefits than nitrogen in only one form and the increase in price for this advantage is very moderate. If one works out average reasonable mixtures of superphosphate and sulphate of ammonia, one will find that the farmer is always paying about £2 15*s.* for the work done in mixing, bagging, etc. Whether it is worth his while to pay this price depends upon the magnitude of his orders and the facilities which he possesses on his own farm for doing the mixing himself, a subject which is discussed again under the heading of Storage of Fertilizers, p. 197.

In reviewing the whole subject of the variations of these manures, it will be noted that, except for sulphate of ammonia, the zero price of fertilizers is high, varying from £2 to £4. It would be more convenient if the zero price of compound manures had been placed rather higher, so as to avoid the necessity of having a duplicate system of unit prices, but there is something to be said for the arrangement

that has been adopted. If the zero price of compound manures included all the expenses, it would not be possible to put it lower than £5, and then there would be a difficulty in producing the higher grades of manure on such a scale. It will certainly always be to the interest of the farmer to purchase the higher grades in fertilizers; it is on very rare occasions that the cost of the manufacture of these articles is anything like proportionately high, whilst the farmer invariably saves the cost of cartage. In these days of high prices of labour, this consideration is becoming more and more important, and manures containing only low percentages of useful ingredients should be looked upon as articles of doubtful utility.

Storage of Fertilizers.—At the works where fertilizers are compounded, the products of manufacture are generally stored in large heaps. Many of the materials are hygroscopic and sufficient care is seldom devoted to keeping them dry. It frequently happens that the works are situated on the banks of a river, the damp air from which makes the manures moist on any fresh-cut surface. Every effort should therefore be made to avoid, as far as possible, mischief from this source. Overhead cranes and transporters are extremely valuable for moving the materials from one part of the works to another. In any case much hand labour must be expended, as it is impracticable to dispense with barrows and shovels. The use of elevating barrows to raise sacks fron floor to cart level helps in handling these substances, and a simple rope and block tackle may also assist, but in any case there is a very heavy expenditure in handling. Fertilizers are often carried some considerable distance by rail, and ten or twelve shillings per ton is, on the average, expended in this way. Transport costs are reduced when railway waggons can be filled, hence 5 or 10 ton loads obtain favourable terms. The transport from the railway station to the farm is usually carried out by the farmer's own carts, and may add another *7s. 6d.* per ton to the cost. On its arrival at the farm, the material undergoes further handling. Of course the farmer would like to have the material carted

straight on to the field where he wants to use it, and when this can be arranged it is quite well worth the farmer's while to pay a few shillings per ton extra for the material. It is this convenience to the farmer which is largely responsible for the difference in price at different seasons. In common practice much of the material is put into store, though the storage capacity on many farms is insufficient. Where a proper manure shed exists it is sometimes used for only two or three months in the spring and early summer, but if the manure shed be properly constructed it can be used at other periods, either as an implement shed, a turnip house, or even as a cart shed. On a small farm the presence of any special place of this kind may be regarded as a luxury, but, on a homestead managing several hundreds of acres, a properly constructed manure shed cannot very well be dispensed with. On farms of considerable magnitude the farmer will frequently desire to prepare mixtures found by experience to be suited to his land. Such a procedure involves a fairly roomy place, otherwise the operation of mixing will be very inefficiently performed. If the mixing of several manures be carried out by barrow, spade and riddle (see p. 179), a floor space of at least 200 sq. ft. is necessary, in addition to the space occupied by the manures stored in sacks. In any shed the different fertilizing materials must be kept apart, otherwise hopeless confusion results. The size of a manure shed depends upon the degree of high farming which is carried out on the farm for which the fertilizers are required. It is a great convenience if the shed either permits a cart to enter, or is built at a slightly higher level than the road, so that a cart can be backed up against it, and thus avoid the frequent raising or lowering of sacks between cart and floor level. A rope and block tackle may be suspended from the roof, so as to permit the easy removal of sacks from one part of the shed to another. If possible, roof lights are desirable, but in any case the place should be well lighted; otherwise mistakes are very liable to occur when the attempt is made, in a dim light, to decipher written instructions, often creased and fouled by use. Where a great variety of crops is grown

or stock fed, the shed will be in active use for the greater part of the year. If there is much grass land which is frequently manured with basic slag, there will always be a considerable store of basic slag in the shed during the autumn months, whilst the chief portion of the superphosphate and sulphate of ammonia will be in store in the early spring months, hence there will not be the same amount of time during which the shed is empty. Where sulphate of ammonia is used largely for top dressing wheat in autumn and spring and where hay is top dressed in the early summer, some store of this material is kept all the year round. Where there is a great variation in treatment in this way, it is convenient to have two doors into the manure shed, so that the two halves can be worked at different seasons without confusion.

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SECTION II.—THE DISTRIBUTION OF FERTILIZERS OVER ROTATIONS OF CROPS

THE practice of growing crops in rotation has prevailed from very ancient times, but it is only during the last two centuries that the varied and extended rotations now familiar have been extensively practised. In very primitive times the forest dwellers burnt down a small portion of forest, sowed grain on the ashes, and, after exhausting their little field in the course of ten years, moved to another part of the forest and repeated the process. The plot of ground which they had left, as being no longer valuable to them, was quite well suited for forest reproduction, and soon grew trees, so that these primitive men of prehistoric times possessed a rotation of ten years' grain and fifty years' scantling and small timber.

Of the more well-defined forms of rotation the oldest known system was a simple two-course of grain and bare fallow in alternate years. The Romans, however, had instituted a three-course rotation of bare fallow, wheat and beans, which they introduced into England with their conquest. Whilst in the British Isles this three-course rotation appears to have been continued, no further progress was made until the beginning of the eighteenth century, when Viscount Townshend introduced the famous Norfolk four-course rotation, which included in succession wheat, turnips, barley and clover. From that time until now many new rotations, varied to suit local conditions, have been established throughout Great Britain. To obtain the largest amount of profit and the greatest yields, with the least possible exhaustion of the soil, are objects which every farmer has in view, and it has become a well-established rule that under ordinary conditions some system of rotation is the best method of obtaining those ends. It is true, that at Rothamsted, many crops have been grown continuously by the expenditure of much

manure, labour and risk of injury from insect pests and fungoid diseases. In addition to the disadvantages of continuous cultivation as regards cost of labour and susceptibility to disease, there are also many advantages in crop rotations owing to the different habits of plants in their root systems and in the kinds of fertilizing materials which they extract from the soil. The bacterial condition of a soil is also much modified by the different phases of the rotation, whilst the continuous repetition of one species limits the variety of bacterial flora. Rotations of crops, intended to produce the largest profits, must vary widely according to the conditions under which farming is practised in the different localities, though there are certain guiding principles which ought not to be lost sight of.

Climate is always a very important consideration when deciding the kind of crop to be grown. Rainfall, exposure to winds and range of temperature have a great influence on the system of farming. The important mangold crop, for example, gives very high yields in the southern counties of England, but only moderate crops are grown on the best soils in the northern counties, and less would be grown there if yield was the only consideration. A small quantity of mangolds is very convenient on a farm, since they keep well over the winter and are available at a time when the softer turnips and swedes have become exhausted. In the cool and damp climates of the more northern parts of the British Isles, wheat takes longer to ripen than in the southern counties, and very much longer than in the sunny climate of Southern France. The long days of Northern Canada permit continuous growth with a corresponding diminution in the number of days from seed time to harvest. The result of this delayed ripening in the British Isles is a softer and inferior wheat of greater water content and lower milling value. Great improvements have taken place in varieties of wheat during recent years, so that we may hope that some of this inferiority of British wheat may pass away. Oats and turnips flourish in cool and moist climates, and are therefore particularly suited to the western parts of the

British Isles. All the damper parts of the British Isles are specially adapted to the growth of forage crops, although the development of full crops of these materials is only possible with very liberal allowances of artificial manures. Cereals attain their best results, both in quality and quantity, on the drier eastern shores, although occasional droughts are only rendered harmless by the judicious use of stimulating nitrogenous fertilizers. It is in the warmer and sunnier parts of the southern counties that clover plants flourish to their greatest extent, but the sturdiness of some varieties, such as wild white clover, have enabled the northern counties to obtain comparable results.

The influence of soil is only second to that of climate. Freshly reclaimed peat soils are suitable only to a few crops, such as oats, potatoes, cabbages and rye grass. Newly ploughed up land of a black humus character has also similar limitations, and great care should be taken in ploughing up old grass land, partly because of the large amount of organic matter contained and partly owing to the difficulty of inducing the soil to settle down. A stiff clay, free from excessive amounts of humus, behaves better, and wheat, beans, cabbages and mangolds do well on this type of land, but on the heavy clays carrots and barley are very difficult to grow, while potatoes and turnips can only be obtained by much cultivation and manure. Loam soils have the advantage of being adapted to the cultivation of all crops; it is only on these types of land that a rigid adoption of any definite system of rotation can safely be pursued. The chalk soils of the Downs give poor yields of oats, potatoes and grass, but clover, peas, vetches and other leguminous plants give good returns on such soils.

Demand and market price take precedence over almost all other considerations in deciding the system of farming to be adopted. In certain favourable situations, where there is a flourishing industrial market and a soil of naturally good character situated over limestone strata, very high rents are obtained. Even £5 per acre may be a fair rent, if large and heavy crops of early potatoes can be grown year

after year. Very important points in the consideration of any rotation is the reduction of labour costs and the greater healthiness and productivity of the crops obtained. A rotation allows an economy of labour because it secures the steady work of the labourers at all times of the year, with neither periods of overwork nor times of idleness. The more complex the rotation, and the greater the variety of crops grown, the more nearly can this ideal be attained; seed time and harvest will extend over much longer periods with many crops than with few, and the ratio of the number of labourers employed to the yield of the crops obtained will be reduced; risks of heavy fluctuation in price will become lower, since, however bad may be the outlook for one crop, compensation is obtained from some other more successful crop. The needs of the live stock must also be taken into account in fixing the method of farming and the system of manuring applied; suitable food must be provided for the cattle all the year round, and this ought to be mainly grown on the farm concerned. Of the actual beef and mutton sold off the farm, at least one-half ought to have resulted from home-grown foods. It is from these home-grown foods that the chief profit is obtained, and it is the manure bill rather than the cake bill that should flatter the farmer's pride.

Stocks of dairy cattle in particular require ample provision of fodder and roots during the winter. They also require a considerable amount of grazing ground to provide them with exercise and feeding during the whole year. Phosphatic fertilizers are especially valuable in maintaining the growth of grass late into the winter. Pastures fertilized with phosphates recover quickly from adverse seasons.

It is difficult in practice to put all such principles into effect, as local considerations and prices may prevent their application in detail. The proper use of artificial manures gives a much greater scope for management of those details. To avoid disease the interval of years between two identical crops should be as long as possible. By alternating one cereal with another, and one root crop with another, much can be done in this direction. Weeds promote disease, and

should be kept down by the frequent use of cleaning or smother crops. Fertilizers suit weeds as well as economic crops, and much of their fertilizing value may be lost unless weeds can be removed either by cleaning or smothering.

The Four-Course Rotation.—The best known rotation is the Norfolk four-course, introduced from Flanders in the early part of the eighteenth century. The common four-course rotation consists of turnips, barley, clover and wheat. Where climatic and soil conditions interfere with the growth of wheat, oats may take its place, or replace the barley crop, where the soil is not in a sufficiently fine condition to give a good barley plant. The four-course rotation receives for the turnip or swede crop about 15 tons of farmyard manure per acre, 5 cwt. of superphosphate and ½ cwt. of sulphate of ammonia, with, on lighter soils, ½ cwt. muriate of potash in addition. As all these manures require to be placed in drills, there is no difficulty in using one of the compound manures alluded to on p. 185.

The second year's crop—barley—usually receives no manure at all. In the barley is sown rye grass and clover, or some similar mixture, which, after the barley has been removed, receives dressings of about 2 cwt. superphosphate, ½ cwt. sulphate of ammonia and ½ cwt. muriate of potash. The sulphate of ammonia may be kept back until later and divided between two top dressings, one in the early spring and one later on before the hay ripens. It is distinctly advantageous in this case to keep the sulphate of ammonia distinct, because the farmer can then take the opportunity of correcting for climatic conditions. Sulphate of ammonia, like all other nitrogenous manures, stimulates feeble plants whatever may be the cause of their unsatisfactory growth.

The third year's crop—clover—may receive a small dressing of about ½ cwt. of sulphate of ammonia, a part of which may be kept back to be applied at a later period of growth. Where the land is in poor condition, or the farmyard manure rather short in quantity, the amount of sulphate of ammonia may be increased with advantage. In many variations of this rotation, potatoes take the place of roots,

and the clover may be replaced by one, two, or three years' seeds mixture, consisting of various grasses, with red clover if it is for a short period, and wild white clover if it is intended to last out for three years. In very poor lands this period may be even increased by cutting hay for two years and grazing subsequently for several years. On rather richer lands wheat may be taken after the rotation previous to barley. Where the hay crop is extended it is desirable that this crop should receive more generous manuring, especially with phosphates; where the land is deficient in lime it is advantageous at this period to use 8–10 cwt. of slag. On light lands, especially those in poor condition, some sulphate of ammonia should be applied to the barley crop and some potash manure used for the hay crop. In the experiments on rotations at Cockle Park, Northumberland, good results have been obtained by using all the farmyard manure for the cereal crop, and all the artificials for the hay crop. In this case the hay received 25 lbs. of nitrogen, 75 lbs. of phosphoric acid and 50 lbs. of potash per acre, which could also be supplied by using 7 cwt. of a mixed fertilizer, containing about 3¼% of nitrogen, 21% of calcium phosphate and 6½% of potash.

On very heavy clay soils rotations may follow the old three-course system of wheat, beans and bare fallow, or its modern improvement of replacing the bare fallow by a turnip crop, or a smother crop, rape, cabbage, tares, etc. In the southern counties of England, where the summers are warmer and longer than in the other parts of Great Britain, an improvement has been made by introducing a catch crop during the winter after wheat and before turnips. This catch crop of tares or rape is generously manured with full supplies of superphosphate, sulphate of ammonia and potash salts, and is consumed on the ground by sheep in the following spring. This system works very well in the South Downs, where sheep are kept on the higher levels for grazing, taken down in the winter to the low-lying fields of vetches or other green fodder, which provide the ewes and lambs with a plentiful supply of food in the early months

of the year. The trampling of sheep consolidates the soil, which is usually light and stony, and provides much manure for the subsequent turnip crop. Thus much of the farmyard manure used for the turnip crop in other parts of the country is supplied on the spot by the sheep.

A modification of the Norfolk four-course rotation, which is often known as the East Lothian rotation, consists of seeds, barley, hay, oats, potatoes or beans, and in the sixth year wheat. It will be noticed that the cereals are varied, although frequent, and that either a cleaning crop or nitrogen collecting crop, like beans, is introduced previous to the wheat. Here, again, the general principles are that most of the farmyard manure goes on to the turnips, the barley getting little, the seeds getting heavy dressings of superphosphate, and the potatoes and beans being well manured with artificials as well. Such a system has the great advantage of distributing the labour well over the different parts of the rotation. Further possible improvements in the existing systems of rotation in the British Isles seem chiefly to lie in some extension of the system of catch cropping. Catch crops, however, require an extensive rainfall, which is more likely to be obtained on the western side of the British Isles than on the east. Catch cropping requires extensive fertilizing, and needs considerable quantities of sulphate of ammonia and superphosphate to produce its best results. Further improvements of existing rotations will mainly lie in the direction of a larger production of leguminous crops, so that nitrogen may be added to the soil after it has been collected by these crops from the air. Further improvements will also probably consist in the development of strains and varieties of seed which will be more capable of resisting insect enemies and fungoid disease.

For allotment and garden crops it is found beneficial to practise some system of change, so that the same kind of crop does not occupy the same piece of ground on two successive years. Owing to the small area and the large variety of crops, it is almost impossible to practise any definite system of rotation. In many gardens, especially

those of the cottage type, the potato holds a pre-eminent place, and may be planted on one half of the garden in each alternate year, the other portion of the garden being devoted to a miscellaneous collection of vegetables. In opening up new ground for such gardens, it is best to dress such grass, rubbish or weeds as may occur at the surface, with lime and basic slag. If one has to bury turf, one may as well bury good turf as bad turf. The land should then be double dug, trenched or bastard trenched, and the turf buried at the bottom. If possible some good manure should be buried along with it, and potatoes grown in the first year. It is not usually necessary to apply very much nitrogen or potash manure in the first year, although if the soil be rather light a little sulphate of potash will do good to the potatoes. After the potatoes have been taken away the land should be well forked over and manured with basic slag; mixed vegetables are grown in the second year. All excepting the peas and beans may be top dressed with sulphate of ammonia, and on light and calcareous soils the top dressing may be a mixture of superphosphate, sulphate of ammonia, potash salts and a little common salt (sodium chloride).

Little direct use of fertilizer is practicable in ordinary forestry work; in the forestry nursery, however, there is some room for artificial fertilizers. The land should first of all be drained and treated with basic slag, and perhaps lime in addition, depending upon the nature of the soil and the class of stock it is proposed to raise. Farmyard manure should also be dug in. Potatoes should then be grown; after the removal of the potatoes the land can be converted into an ordinary forest nursery. If it is necessary to use some rather poor sandy soil as a nursery, potash manures should not be omitted; on light soils much organic matter in the form of leaf litter should be used.

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Section III.—MANURES FOR SPECIAL SOILS AND CLIMATES

Light Soils.—Light soils are, as a rule, deficient in potash, nitrogen and humus. Their water-retaining powers are very poor, they readily permit the fertilizers used to drain away, and sometimes they are deficient in lime and phosphates as well. The manures most likely to be successful are superphosphate, sulphate of ammonia and either chloride or sulphate of potash. Farmyard manure is almost invariably essential. Such soils are easy to plough and dig, but are difficult to maintain in high fertility, due to their low retentive power; it is sometimes not profitable to use large dressings of fertilizers since the losses by drainage are heavy. Very much waste land is uncultivated because it is too dry. A soil which is very light and sandy may be a fine fertile soil on the west coast, and uncultivated on the east coast, because of the difference in rainfall. Where there is an ample supply of underground water many of these light soils are very prolific. At the base of the South Downs there are many fields which consist largely of flints and coarse particles brought down by washing from the Downs, but water is obtainable within a foot or so of the surface. This underground water originates from the higher land in the South Downs and, in the process of making its way to the sea, it supplies water for the growth of all plants, even though the physical properties of the soil may not be very good. As there is no heavy leaching of fertilizing ingredients, chemical fertilizers may be safely used in large amounts.

Where there are no natural advantages of high rainfall, irrigation is necessary for supplying the required water. Before the dawn of history, elaborate networks of irrigation canals in Mesopotamia and Persia were fully established. When climate permits, as it does in many parts of the

sub-tropical regions, irrigation may enable the cultivator to produce two or three crops in a year; on such lands irrigation is extremely profitable. In the British Isles irrigation has presented too many difficulties to be undertaken on any large scale; some slight efforts are made in the Fenland districts, where excessive water is pumped up into high-level canals and a deficiency of water is remedied by merely reversing the mills. The difficulty of lack of water is generally surmounted by making the most of the water in the soil. Organic manures, such as farmyard manure, increase the retaining power of the soil, and therefore spread the water supply over longer periods. Systems of cultivation on the surface prevent excessive evaporation of water. The use of stimulating manures like sulphate of ammonia and nitrate of soda at critical times does much to mitigate the evils due to a lack of water. To some extent manure may be said to take the place of water, since plants that are well manured do not require as high a proportion of water transpired to plant tissue formed. The soluble fertilizers, such as superphosphate, sulphate of ammonia and potash salts, are those that have proved most useful on light lands afflicted with drought. Some light soils, however, are deficient in lime, when it may be better to use basic slag instead of superphosphate, but lime and basic slag must be used sparingly on light dry soils. On light, dry soils, lime destroys the organic matter which is commonly deficient, and modifies the physical conditions till the soil becomes still drier. In such cases it is better to use ground limestone. The method commonly adopted to consolidate these light soils is to grow a green crop to be eaten by sheep, so that the soil becomes firmer and very much more retentive. Whilst much has been done during the last hundred years to overcome the wetness of soils, it cannot be said that the difficulties of overcoming dryness have been tackled quite so fully.

Sulphate of ammonia, when used on light lands, may produce results similar to those discovered at the Royal Agricultural Experimental Station at Woburn, where, by its excessive use, lime has been so completely removed from

the soil as to render it infertile. By the addition of extra lime the fertility is recovered. There is little doubt that the acidity of such soils resulting from sulphate of ammonia is produced largely by the growth of moulds; the use of lime discourages these, and promotes more healthy bacterial life. Nitrate of soda, when used on light soils, has been found at Woburn to produce similar results, although the causes are certainly not identical. One of the reasons, apparently, why nitrate of soda has been unsatisfactory on these light soils is that when the nitrogen has been used by the plant, the soda is left behind. In the presence of soda clay becomes colloidal, and in a soil of open structure such colloidal solutions of clay readily drain away deep down into the subsoil; consequently the clay particles are carried away from the surface and deposited deep down in the soil. If the total amount of clay particles is small, the whole stock of clay may be removed from the surface, which becomes absolutely dry within a few hours of the cessation of rain, and the germination of seeds becomes almost impossible. The behaviour of calcium cyanamide in sandy soils may follow more than one method of procedure. Calcium cyanamide readily breaks down, yielding ammonia, when it nitrifies in the usual way. Experimental results at Rothamsted point to an almost quantitative conversion of cyanamide into nitrates. Calcium cyanamide, however, may contain a certain amount of dicyanodiamide, which checks nitrification in the soil.

Superphosphate is a favourite fertilizer for the lighter soils. These light soils are easily worked, and a readily soluble fertilizer like superphosphate need not be applied early. The ready solubility of superphosphate enables it to be used even as a top dressing. When labour is short, it is a great advantage to be able to leave fertilizing with superphosphate until a late date. Superphosphate is not a suitable fertilizer unless the soil contains a moderate amount of lime. Alternations in the use of basic slag and superphosphate are therefore a satisfactory solution of this difficulty. Basic slag has often given excellent results on

light soils, although its slower action necessitates its use at an earlier date. On light soils it is often necessary to use potash as well as basic slag. Rothamsted results show that the use of magnesium and sodium sulphate has an important action on crop returns. It seems highly probable that some of the calcium sulphate in superphosphate may serve a similar purpose. Potash manures are especially valuable on light soils. It is rare to find a light soil so well supplied with potash as not to need potash manuring, but ordinary farmyard manure, if well preserved, is fairly rich in potash, and many farms depend largely upon this source of potash. Where a farm contains some fields that are heavy and some that are light, the fertilizing ingredients which the hay removes from the heavy lands find their way through the beasts to the light arable portion of the farm. Where there is a sufficient rainfall, light soils can produce large flushes of green manure, provided they are liberally supplied with all fertilizing materials.

Manures and Heavy Lands.—Heavy soils are, for the most part, poor in lime and phosphates, although they are relatively rich in potash and nitrogen. When used for arable purposes, farmyard manure is necessary to break up the soil into a more open condition, suitable for cultivation. The great success of the application of basic slag to heavy soils may be attributed to their extreme poverty in phosphorus. Many heavy soils have been grazed for centuries, and considerable amounts of phosphates and lime have been removed in the bones of the cattle that have fed there. Relatively, much less other fertilizing material is removed, since nitrogen accumulates in the soil by the growth of clover, and the soils are relatively rich in potash, of which 99% of that eaten is returned to the soil by the cattle. Ashes and other coarse granular material do much to improve this type of soil. Such lands are undoubtedly hard to plough, but give good returns for the fertilizers that are expended upon them. If they are excessively wet, they may be economically drained by the use of the mole drain plough. Without any draining much can be done to dry out these heavy wet lands by encouraging vigorous vegetation. By the use

of basic slag on such soils clovers are encouraged to grow, and the increased production of vegetation includes increased transpiration by foliage, which is only possible with increased root activity, resulting in the removal of water from the soil. At the same time, the clover roots open up the surface soil, and do much to improve its physical properties. Sometimes this heavy soil is wet because it lies at a lower level than the surrounding farms; in that case it is the cultivation of the surrounding farms that should be improved. By more intensive systems of cultivation, wet, heavy land can often be completely reclaimed.

For heavy land sulphate of ammonia is not always suitable, although as a top dressing it is valuable enough. Nitrate of soda is very commonly used for the mangold crop, but is not a fertilizer particularly well suited to heavy soils, as it is apt to leave soda behind and render the soils very sticky. Basic slag is the most important manure for heavy lands; superphosphate and lime will also do very well, but the expense is greater, and as heavy lands are expensive lands to manage under any circumstances, this is a serious item; potash manures are rarely of much value, since fairly liberal dressings of farmyard manure are generally applied.

Peaty Soils.—Peaty soils are usually very wet and retain water easily; they may dry out rapidly on the surface, but they are apt to be sour, and make bad seed beds. Lime and basic slag are necessary for starting cultivation on these peaty soils, although, after plants have been established, attention should be paid to more expensive fertilizers. Large crops of potatoes have been obtained on these kinds of soil, but continuous attention is needed to prevent peaty soils from returning to their original infertile character. Drainage is often an essential preliminary to cultivation. Sulphate of ammonia and nitrate of soda on these soils are very valuable as top dressings. After basic slag and lime have been used, fairly liberal mixed manures, superphosphate, sulphate of ammonia and potash salts may be employed with success. In the Fen district it has been found necessary to keep water out of the land by draining on a large scale.

Calcareous Soils.—Chalk soils or soils situated upon limestone formations are well suited to the use of superphosphates, sulphate of ammonia and potash manure salts. By long cultivation, the surface of these soils has often been so completely denuded of its lime, that it may become necessary to make applications of calcareous fertilizers. As lime, chalk or ground limestone are easily obtainable in the district, there is no great difficulty or expense attached to this operation. Basic slag may also be used in these soils when the surface lime has been washed away. Somerville, at Poverty Bottom, has obtained some striking results in the use of basic slag on chalk soils. Nearly all of the artificial fertilizers, as well as farmyard manure, do well on chalk soils. Nitrification proceeds readily, and there is no fear of acid conditions prevailing.

Where the opposite condition of affairs prevails, and the soil is particularly deficient in lime, the remedy is to apply lime as a manure. A great deficiency of lime in a soil is frequently recognizable by the presence of the weed spurry on the lighter soils or sorrel on the heavier lands.

Cold Climates.—In most of the cold climates and the more northerly part of the temperate zones, long winters prevail, during which there is a cessation of agricultural enterprise. Owing to the long periods of bad growing weather, some stimulating manures are often required. When wheat is grown, the land should be kept in a good condition and well supplied with phosphates, whilst top dressings of sulphate of ammonia may be used either during the winter or spring. Lime in some form or another is often very necessary, because of the difficulties of nitrification. The speed of nitrification in the soil depends, among other things, upon the temperature and the prevalence of lime compounds. As the temperature is low, it is necessary to see that the other accelerents of nitrification are not deficient. Assisted by good soil conditions Canada is able to push the wheat belt far up to the north, whilst in the British Isles wheat growing becomes of less and less importance as one proceeds in a northerly direction.

Tropical Climates.—A characteristic of all tropical regions is the great rapidity of nitrification in the soil. Nitrates are very easily lost by drainage should the rainfall be heavy, hence sulphate of ammonia and organic manures are often very valuable. As the climate induces rapid ripening, there is not the need for the use of phosphates as is felt in colder climates, though there are many soils which need considerable amounts of phosphatic fertilizers. Phosphates always need replacing, when they have been removed from certain areas since prehistoric times by excessive grazing. The results of experiments in many tropical places show that where the climate and soil lend themselves to large crops, heavy applications of fertilizers are often extremely profitable, but where the crops are not in any case large the use of these expensive manures is often economically unjustifiable. For example, the yield of maize on one experimental unmanured plot was comparatively low and no improvement was induced by the introduction of superphosphate on a parallel plot; in a district where the unmanured plot was of a somewhat more fertile nature, owing to the soil and climatic conditions, the use of artificial manures was very striking. Where the water supply is good, very large crops can be obtained in warm climates, and where the amount of water is insufficient small top dressings of easily soluble fertilizers may help the crop over a difficult and droughty time. Drought causes premature ripening; the use of sulphate of ammonia in such cases, by extending the period of growth, may produce very valuable results.

Wet and Dry Climates.—The relative effects of wet and dry years on crop yields are shown admirably by Hall in the Rothamsted experiments. A comparison of a wet year with a dry year and with an average of many years, on the wheat field at Rothamsted, shows that in a dry season farmyard manure is very good indeed, but that in a wet season the minerals show up well. It is very striking in these experiments how materials that are not considered of high manurial value produced special results in the wet years. In the wet year of 1879 sulphate of soda and sulphate of

magnesia produced far greater results than they did in the dry year of 1893, whilst sulphate of potash was rather better in the dry year than in the wet year. The ammonia compounds come out very well in the abnormal years. In a wet season, when there is plenty of water, the farmyard manure loses its pre-eminent position, so that many forms of artificial manures are equal to, and sometimes superior to, farmyard manure. On the other hand, during the dry years farmyard manure easily heads the list. With wet climates and open soils, soluble manures very easily wash away, and it is hence necessary to supply these at intervals as top dressings. Dry climates with retentive soils lose very little, and the soluble manures are not easily lost. On the other hand, it cannot be said that the light soils with dry climates particularly need the less soluble fertilizers. Where both soil and climate are dry, it is necessary to use soluble fertilizers to economize the water that is so deficient.

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Section IV.—MANURES SUITED FOR SPECIAL CROPS

In discussing the application of fertilizers to crops, conclusions as to the correct method of fertilizing cannot be drawn unless we take into account the place which the crop occupies in the rotation adopted, as has been shown on p. 199. The manuring to be adopted on any farm must be regarded as a whole, and not merely with reference to one particular crop. The system most suited to the farm depends upon many other factors than the crop grown at the moment. It is easy to prescribe a manure suitable for one particular crop, but little advantage results unless there is some knowledge of the general manner in which the farm is conducted. The style of farming and the amount of fertilizer that can be profitably employed are very largely dictated by considerations of labour, rent, railway facilities, proximity to markets and other practical conditions. The farmer of new land uses little fertilizer because he is living upon capital originally stored in the virgin soil. In many parts of Great Britain a conservative system of farming is maintained in which the land has already attained a certain condition, and will continue to yield average crops with little outside aid in the form of purchased fertilizers and foods. On the other hand, the intensive farmer is using his land as a manufacturer uses his plant, bringing in large quantities of raw material and steadily increasing his production from year to year. On allotment lands, that have sprung up during the war, much of the land taken over was in the worst possible condition, but, with the expenditure of much labour and fertilizers land which produced no food has given good results in a very short interval of time. The reason why this transformation was practicable was because the value of the labour expended was not counted. Where the allotment holder engaged a

skilled hand to put in much work upon his land, his balance sheet, if he had ever produced any, would have been an illustration of mere bankruptcy. To grow everything and be self-supporting even on the best land is compatible with only very low average yields, which can only be raised by an external supply of fertilizer. Fertilizers often do less to feed the crop directly than to maintain the fertility of the land. At the present time it is often necessary to raise the fertility of a land above its previous level, and this can only be done by the generous application of fertilizers, some of which may not produce their full return for several years.

The Cereals.—Wheat, in a typical four-course rotation, follows the ploughed up-lee from the previous hay crop, and generally derives as much nitrogen as it requires from the residues which are left in the soil by the clover or other leguminous plants which formed a large part of the herbage which produced the hay. Where there has been "a bad take of clover in the seeds," the amount of nitrogen collected may be quite insufficient for the needs of the wheat plants, and top dressings of sulphate of ammonia are very valuable. In many cases, especially in the northern parts of the country, oats are now substituted for wheat after lee, since grazing may be carried on much later into the winter before the land is broken up, there is less pressure of work in the later autumn and early winter months, and winter frosts have cleaned the land from insect pests and weeds. Where a top dressing is necessary, from ½ cwt. to 1½ cwt. of sulphate of ammonia is used, preferably spread over two or three dressings. When wheat follows liberally manured mangolds, very little more fertilizer is required. Where wheat or other cereals are grown continuously on the same land, liberal supplies of both phosphates and nitrogen will be needed, and 2–3 cwt. of superphosphate or basic slag, with 2–3 cwt. of nitrate of soda or sulphate of ammonia as top dressings should be applied. As wheat will very rarely be grown on light soils, it is not necessary to consider potash fertilizers. Nitrate of lime and nitrate of ammonia may also be used as top dressings for these crops, but calcium cyanamide is not

so suitable. Recent trials at Rothamsted have given the best general results with sulphate of ammonia on barley. Barley is grown under somewhat different conditions of tilth, but it may follow wheat, and form a second, or even a third, white straw crop after roots or clover lee. In such cases the high condition of the soil is taken out by the first crop of wheat, and there will be little readily available nitrogen left. Good malting barley, which fetches the highest prices, contains little nitrogen, and nitrogen manures must be applied sparingly; but impoverished soils will not yield good barley. It is desirable that the nitrogen should come from the condition of the land rather than from very soluble manures like sulphate of ammonia. Phosphates are very essential for barley, and therefore dressings of superphosphate may safely be used. Where there is a risk of delayed ripening, a mixture of superphosphate and sulphate of ammonia may be applied; this gives the young plant an easy start, and enables it to grow away without check. Sodium chloride is sometimes used on light land for the barley crop. Rape dust has also proved very useful where small quantities of nitrogen are needed for barley. A mixture of 1 cwt. of superphosphate and 1 cwt. of steamed bone flour provides another very suitable manure; a little sulphate of potash may be added if the soil is very light. When barley follows roots which have been very highly manured, especially when the roots have been folded off by sheep, the land is already too rich in nitrogen for barley, and therefore no more nitrogen should be used, although superphosphate may sometimes be applied under these conditions. Where oats are grown on poor land, 2 cwt. of superphosphate and 1 cwt. of sulphate of ammonia is a good mixture, but basic slag may often take the part of superphosphate with advantage, since oats suffer when grown on sour soils.

Root Crops.—The greater part of the manure that is made on the farm is applied to the root crops (see p. 205), although in the southern parts of England it is frequently applied to the hay crop instead. Large crops of roots or silage are needed for the maintenance of farm stock. Generous

manuring for root crops is profitable, and the fertilizing ingredients in the crop so obtained return to the manure heap once more, and build up the whole fertility of the farm. Starving the root crops or green fodder is a very bad system of farming. The amount of nitrogen in manure that the swede crop can take is limited, and about ¾ cwt. of sulphate of ammonia, in addition to farmyard manure, is as much as it is worth giving. In addition 4–5 cwt. of basic slag or superphosphate may be used. Where no farmyard manure is available, 4 cwt. of superphosphate, 2 cwt. of fish meal and ½ cwt. of sulphate of ammonia is a good dressing. The sulphate of ammonia may be applied as a top dressing at the time the plants are singled. Care must always be taken with regard to turnips and swedes that the land is not deficient in lime, and it is therefore good policy to use basic slag in place of superphosphate on some occasions. Finely ground rock phosphates do remarkably well for the swede crop (see p. 187), and it is therefore highly probable that mixtures containing much insoluble phosphate and a little soluble phosphate will, in the future, become more popular. Roots, cabbages or other fodder crops which are grown on an excessive amount of nitrogen, make inferior foods.

Mangolds.—Mangolds respond to very large quantities of nitrogen, and nitrate of soda is particularly valuable; potash is also necessary, but phosphoric acid is of less importance. Resulting from the large amount of water needed for growth, it is necessary that much farmyard manure should be used to obtain a good soil texture. Farmyard manure is not sufficiently rich in potash, and extra potash fertilizers are almost always necessary. With 15 tons of farmyard manure per acre, 3–4 cwt. of kainit and 1–2 cwt. of fish guano should be sufficient. After singling, top dressings of nitrate of soda and salt may be used to the extent of 2–3 cwt. Slag has proved better than superphosphate in the northern counties; in the midlands, superphosphate has produced the better results. On the light soils at Woburn up to 6 cwt. of salt per acre has proved beneficial, and even quantities as large as 10 cwt. of salt per acre have been used.

Potatoes.—Potatoes are grown under such a great variety of circumstances that it is not possible to lay down any general rules for manuring. Potatoes sometimes form a portion of the general rotation, replacing turnips or mangolds. In other cases, where there is a good market, they are grown more frequently. In Dunbar little farmyard manure is used, but potatoes are grown after clover, which has been grazed with cake and corn. By the use of more phosphatic fertilizers on the clover, probably much of the expense of cake and corn could be avoided. With any large excess of nitrogen, potato plants become more susceptible to disease and the tubers turn a bad colour on boiling.

Remarks are often made about manures which set up an alkaline reaction, and facilitate attacks of potato scab. The author has, however, grown potatoes on experimental plots with as much as 20 tons per acre of lime without any exhibition whatever of potato scab. Similarly, very large dressings of basic slag have failed to produce any signs of potato scab. Although the general opinion of the inadvisability of using lime for potatoes must be respected, potato scab is probably not a primary but a secondary result. Injuries may be done to the potato by wire-worms, millipedes, slugs, and other soil creatures; these wounds, doubtless, render the potato plant susceptible to bacterial attack. The potato is tolerant to a very wide range of soil conditions, and it is quite conceivable that an improvement in the soil conditions might assist the growth of the enemies of the potato more than that of the potato plant. The very large dressing of 20 tons per acre of lime would probably not have made the soil a more convenient resort for insect pests, and may therefore have left the potato more immune from attack. In general, it may be said that very large dressings of farmyard manure are unnecessary, excepting for garden cultivation, where, owing to the much greater depth of soil worked, and the much greater amount of labour put on the land, it is practicable to utilize these larger dressings. Where manure is somewhat short, dressings of 4–5 cwt. to the acre of superphosphate or basic slag, 1–2 cwt. of potash and 1–2 cwt.

of sulphate of ammonia will be sufficient. In Lancashire, where no farmyard manure is used, as much as 6 cwt. of superphosphate, 2 cwt. of muriate of potash and 2½ cwt. of sulphate of ammonia are used, although in most districts muriate of potash is thought inferior to the sulphate for potatoes. In Devonshire it has been observed that large amounts of phosphates and nitrogen are of little value, but that the ordinary dressings of potash may be increased without harm. Where liberal dressings of farmyard manure are obtainable in the northern counties, 10 tons of dung, 1 cwt. sulphate of ammonia, 2 cwt. basic slag and 1½ cwt. superphosphate are recommended. On peaty soils the sulphate of ammonia can be reduced, if not actually dispensed with, but phosphates and potash are generally necessary. On the whole, sulphate of ammonia and superphosphate have proved the most satisfactory fertilizers for potatoes. Nitrate of soda has rarely given good results, but basic slag has proved very advantageous in some districts.

Leguminous Crops.—Under modern conditions of British agriculture, beans only play a small part; generally they come between two straw crops. A little farmyard manure, phosphate and potash may be used, but nitrogenous manures should be left out for this crop in the rotation. Beans are grown very largely for their subsequent beneficial effect upon other crops, and cannot be considered by themselves. About 4 cwt. of basic slag applied to the bean crop may be very successful, but further expenditure of fertilizers is not likely to be repaid.

Clover.—Red clover is a means of supplying the soil with nitrogen derived from the air. As clover cannot be grown continuously on the same land, manurial treatment cannot be considered separately from the rest of the rotation. Even on the best clover soils in the country, clover can rarely be grown more frequently than once in seven or eight years. Lime and potash salts are certainly helpful, and phosphates are good. Clover is nearly always sown in the barley crop and therefore the manure is applied to the barley. It is better, therefore, that the barley crops, and perhaps even

the turnip crops previously, should be well manured with phosphates, leaving merely their residues for the clover. Other leguminous crops like lucerne and sainfoin may be treated in the same way. As lucerne and sainfoin will stand longer than clover, the barley amongst which they were previously sown should be very well manured with phosphates. Top dressings of potash salts may be used, and occasionally a little nitrate of soda to start the young plant in its first stages of growth.

Grass Lands.—Clover by itself is not so satisfactory as in admixture with other vegetation, such as grasses. A grass crop does not consist of a single botanical species, but always includes a great variety of species.

A perpetual competition takes place between the different species, each of which is endeavouring to crowd its neighbours out of the field. The appearance of the pasture is some guide to the type of manure to be used. Creeping bent grass is usually prevalent on heavy lands deficient in phosphates; cocks-foot and brome grass is often to be found on sandy, droughty soils, where potash is necessary. Land laid up for hay with little or no grazing must receive regular manuring. To what extent fertilizers can be expended on this crop depends largely upon the capacity of the district. An instructive contrast of the effects of different climates may be made by comparing the results of Northumberland, at Cockle Park, and those obtained in Hertfordshire, at Rothamsted. Although the unmanured plot in each of the two places gives yields of hay which differ by only 1 cwt. per acre, the best plot at Rothamsted yields 24 cwt. more hay than the best plot at Palace Leas in Cockle Park. Under such circumstances the monetary return could not possibly have any relationship in the two places, since the profits by using fertilizers at Cockle Park are limited so severely by its bleak situation. (See p. 1.)

A comparison of these and similar experiments shows that where climatic conditions preclude the possibility of obtaining bumper crops, the use of farmyard manure and slag give the best hope of profit. Robertson has shown that mineral

rock phosphates may do very well on many hay fields, where, if limited by climatic conditions, the maximum crop obtainable is not very high. On the other hand, where it is possible to raise over three tons of hay per acre, as at Rothamsted, far greater scope for profitable employment of fertilizers exists, and under such conditions complete manures of superphosphates, sulphate of ammonia and potash salts are likely to be profitable.

Pasture.—Pasture removes less from the soil than any other system of farming, but the profits are not sufficiently great to pay for any large expenditure on fertilizers. On pasture, superphosphates, sulphate of ammonia and potash manures are not generally applicable, although there may be many special places where their use is justified. For the bulk of pasture the cheaper manures, like basic slag and rock phosphate, give the best promise of profitable result. Many pastures are only poor land, and cannot afford to pay high prices for fertilizers, but in exceptional cases of rich natural pastures, fertilizing may be taken up in a more generous way. Poor pastures are often dry and deficient in lime and phosphates. In poor pastures basic slag encourages the growth of wild white clover which improves the texture of the soil at no great cost. Where the land is somewhat lighter, dressings of potash salts are often desirable. On thin, sandy soils pasture is difficult to improve, but basic slag, in conjunction with potash, will often do much good on this type of land. On poor, thin chalk soils, superphosphate, sulphate of ammonia and kainit sometimes produce striking results, but it is difficult to make much profit, owing to the expense of the fertilizers. More profitable returns have been made with basic slag, as in Somerville's well-known demonstration at Poverty Bottom. Where there is a ready sale for milk superphosphates have given good results. At Harper Adams Agricultural College superphosphate has proved very profitable for milk production. Most of the great difficulties of treatment of grass land occur in the drier half of the British Isles. Where there is ample rainfall there is much more scope for the use of complete artificial fertilizers.

Forage.—The difficulties and expense of making hay, and the heavy cost of root growing, combined with the equally high cost of labour, are inducing farmers to turn their attention more and more to the production of silage. For this purpose various green crops are grown, which can be loaded into the silo in small amounts at a time without putting any great strain upon available labour. The harvesting is therefore extended over a much longer interval of time. Where it is desirable to obtain large crops of green fodder, fertilizers are very necessary, and generous dressings of superphosphates, sulphate of ammonia and potash salts have usually proved profitable. One of the difficulties of the growth of root crops is the lack of sufficient rainfall in the district, and lack of water will still trouble the man who tries to grow large forage crops.

Golf Courses.—To establish a good surface on clay soils through the green, 5 cwt. of basic slag every few years makes the best foundation; but on the greens, 1 oz. of sulphate of ammonia per square yard once a year is needed to keep down clovers, which make putting erratic; on the fair way clovers are good.

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PART V.—THE FUTURE OF FERTILIZERS

SECTION I.—NEW SOURCES OF FERTILIZERS

Nitrogen Fertilizers.—The better utilization of atmospheric nitrogen may be looked forward to as a means of increasing our supplies of nitrogenous fertilizers. As yet it is too early to form any definite opinion as to which methods will prove the most satisfactory. The use of the electric arc furnace involves much electric power, but, on the other hand, requires only one factory, only two processes, and can easily be worked intermittently. As the whole process is worked entirely by electric power, merely switching off the current stops the whole machine. In the future one may look for some improvement in this process, since undoubtedly many furnaces are faulty, because a large proportion of the air passing through cannot possibly come into contact with the arc. The fears of insufficient electric power to work this process are not altogether justified. Although it is generally considered that water power is essential, yet, as a matter of fact, electric energy obtainable from coal has been sold at very low prices in the county of Durham. The utilization of waste energy has still scope for large future developments; there are innumerable industrial concerns where there is very much waste of heat, which can easily be turned into steam, and thence into electric energy. Where waste heat from coke ovens is procurable, the arc process presents the advantage that electric power can be used to make nitric acid, which is then subsequently combined with by-product ammonia; the ammonium nitrate so formed contains a high percentage of nitrogen and is obtained without adding any outside materials. Up to the present the manufacture of nitric acid by electricity, obtained from waste heat, has made

little progress because more profitable enterprises have been open to those who possessed the necessary machinery. To some extent these developments have been dependent upon war needs, and the future may show a greater temptation to the owners of waste heat to utilize it for the production of nitric acid.

The Haber Process of Synthetic Ammonia.—This process involves many practical difficulties of an engineering type, but it is chemically simple, and is comparatively self-contained. It may be taken almost for granted that the German Badische Anilin Fabrik will install plant outside Germany, and other countries have already produced workable plants, while competition will gradually improve the process. The Haber process claims to be able to produce ammonia very cheaply, and if the difficulties of construction can be surmounted there does not seem to be any reason why this claim should not be made good (see p. 93).

The Cyanamide Process.—This process is more complicated and circuitous than the methods named above, but up to the present more nitrogen has been fixed by this method than by any other. The first product, calcium carbide, is important, as it is used for the production of acetylene; the furnaces producing calcium carbide will therefore be kept in employment, even if nothing further is done. The next step produces calcium cyanamide, a manure which can be used directly on the land. The cyanamide produced can be converted into ammonia, and the ammonia can be converted into ammonium sulphate, or, alternatively, it can easily be oxidized into nitric acid. There is, therefore, a much greater security with this process than the others, since a readier market can be found for all its products. Probably there will remain room for the three different processes. The arc process produces nitric acid directly; the Haber process yields ammonia, which can be oxidized to nitric acid; and the cyanamide process can hold its own under any conditions.

Nitrogen Fixation by Barium Oxide.—Mixtures of barium oxide and carbon, when heated, absorb nitrogen,

with the formation of cyanide and cyanamide of barium, which give off ammonia on passing in steam. Up to the present, little practical use has been made of this method, but in the future it may come into more prominence.

The Serpek Process.—Alumina, carbon and nitrogen give aluminium nitride, which, on treatment with caustic soda, gives ammonia,

$$AlN + 3NaOH = NH_3 + Na_3AlO_3$$

Pure alumina for the manufacture of aluminium can be made in this way. The success of this method is entirely dependent on the market for the pure alumina produced from crude minerals.

By-Product Ammonia.—As time goes on, and greater care is taken of coal, a larger proportion of the nitrogen in coal will be recovered in the form of ammonia. In Great Britain, there is an almost certain decrease in the production of coal, and a further decrease in the consumption, owing to the necessity of cutting down fuel costs. Other parts of the world are, however, increasing their production of coal and coal products. In the manufacture of compound fertilizers, ammonium sulphate will continue to be the most suitable standard article. Ammonium nitrate might be produced, but it is rather doubtful whether much advantage would result, as it is too concentrated for ordinary use on the land, and does not lend itself to mixtures. All the countries engaged in war have invested very large sums of money in nitrogen fixing plant, and many of these may continue to produce nitrogen compounds, so that there should be ample supplies of nitrogen compounds for agricultural and industrial purposes. In estimating the relative values of the different forms of nitrogen products, by-product ammonia always stands out as an article which must be produced, and there is no price so low as to stop its production (see p. 189).

Nitrogen Fixation on the Land.—The fixation of nitrogen in the soil is greatly increased by the growth of leguminous crops, which are encouraged by the employment of phosphatic manures. Much extended development on

these lines should form part of any future national agricultural policy. Large quantities of nitrogen can be fixed in this way, but the nitrogen is not in a very active form, and soluble nitrogen compounds will still be necessary for farming practice. Chemical nitrogen fertilizers will always have the great advantage of serving as a top dressing during critical periods.

Phosphates.—Future discoveries of phosphatic manures may be looked upon as almost certain. Ultimately, further developments in the steel industry will produce an increasing amount of basic slag. There is a tendency to use ores containing little phosphorus at first, but as these become exhausted, poorer ores are consumed, which yield larger amounts of phosphatic slag. No very great improvement in the manufacture of slag can be anticipated from the fertilizing point of view; the general tendency has been to produce basic slag of decreasing solubility. There is some reason to believe that a finer degree of grinding may compensate for the decreasing solubility of these materials.

Potash Fertilizers.—Very promising sources of potash for the future are the flue gases and dusts of blast furnaces, cement kilns, and other industrial operations conducted at very high temperatures. The Scottish blast furnaces, being mostly coal fired, produce less potash than the English coke-fired furnaces. The replacement of coal by coke would result in the increased production of potash. It has been found that by increasing the temperature of the furnaces, or by adding common salt, the amount of potash volatilized is increased many-fold. It seems highly probable that some of the potash which is produced in the blast furnaces comes from the fuel, in which case enquiry should be made into the potash contents of all the different fuels. This is a matter which has hitherto attracted no attention, but the substitution of fuel containing much potash for one containing little, might produce a profound result on the potash yield. The potash from vegetable and kitchen refuse might be rendered available if destructors were modified for the purpose. Wool washings can provide an appreciable amount

of potash. Up to the present the German potash deposits have been allowed to monopolize the whole business of mineral potash. It is by no means certain that there are not many other potash deposits in the world that can be worked equally well; there is no real evidence for or against the opinion that there may be considerable amounts of potash even in the British Isles. The system of working salt measures with the aid of water is the best means of disguising the possible presence of potash, and investigations into this source of potash should be made. Undoubtedly, when the German and French potash deposits are more fully opened up, the world is likely to see substantial increases of potash available for fertilizing purposes. If properly utilized there need be no risk of a glut of potash.

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Section II.—IMPROVEMENTS IN THE MANUFACTURE OF FERTILIZERS

In the superphosphate industry there has been a steady improvement in the composition and physical properties of these fertilizers during many years. Thirty to forty years ago, fertilizers rarely contained more than about 25 % of soluble phosphate, whereas modern samples contain from 30 to 35 %. This improvement has been obtained by better selection of mineral phosphates, and more careful attention to details during the process of manufacture. The increase in the percentage of soluble phosphates has been accompanied by a correspondingly great improvement in the physical properties of the material, which is now usually sold in dry condition. Although the industry was founded in England, the lead has long been lost. Few modern British makers possess the mechanical dens and electric transport of the modern continental factories of Europe, although there is a marked tendency, even among the smaller factories, to utilize some of these modern engineering helps. Not merely is there great hope of increasing the quantities of phosphatic fertilizers used in the British Isles, but the remainder of the British Empire is likely to need much phosphatic manure in future; in Australia alone, large areas are known to be urgently in need of phosphatic manures.

When phosphatic fertilizers were first introduced, the results of the application of soluble forms produced such striking results that the beneficial effects of insoluble forms passed unnoticed. With careful experimental investigation, the benefits resulting from the employment of the more insoluble types became evident, and it is now probable that mixtures of soluble and insoluble phosphates will become popular. While the best farm land is steadily increasing in

fertility, there is much land which has received so little fertilizer that it is still going back. It is on the latter very hungry soil that insoluble phosphates will produce their best results; when the land has acquired a certain condition of fertility, it will no longer respond to the insoluble forms, although it may show excellent results from the application of soluble forms of phosphate. It is also certain that mixtures of nitrogen, partly soluble and partly insoluble, are often better than either alone, although there is no evidence to show that in the case of potash the value of the insoluble forms is more than a small fraction of that of the soluble forms. In the construction of compound fertilizers it would be advantageous if these materials were better standardized than they are at present. Simple mixtures containing the fertilizing ingredients in proportions of round numbers would be better than the odds and ends one often sees quoted. Standard articles containing, say, 1 or 3 % of soluble nitrogen, 1 or 2 % of insoluble nitrogen, 10 % of soluble phosphates, 10 % of insoluble phosphates, and 1, 2 or 3 % of potash would serve practically any ordinary purpose. If half a dozen standard formulæ with even numbered percentages were devised by the manufacturers, it would add much to the popularity and utility of such materials. Fancy names are only misleading, if they attract the ignorant man they repel the intelligent farmer.

Some very marked improvements in manufacture are likely to follow on the recent engineering successes in the recovery of dust of all descriptions. Among the numerous methods that have recently been employed for separating solid and liquid substances from gases which hold them in suspension, may be mentioned the electrical precipitating process designed by Cottrell. If a metallic plate connected to one terminal of a source of high potential is fixed opposite to a needle point, connected to the other terminal of that source, the air particles in the gap will take up a charge of electricity. The solid and liquid particles floating in the gap also become electrified, and are attracted to the plate electrode. The greater the potential difference, the higher the

charge, and the more rapidly will the particles travel. In practice the necessary charge is produced by connecting a source of alternating current to the low-tension terminals of a transformer, the high-tension terminals of which are connected to a mechanical rectifier, which produces a direct current. The receiving electrode connected with the precipitating plate is usually earthed, for convenience and safety. The dust collected on the plate by these means is knocked off by a tapping appliance and transferred to a spiral conveyor, by which it is carried to the store. Much of the dust of high fertilizing value which is produced in grinding machinery may be recovered in this way, as well as many other special flue dusts, for which this type of apparatus has been mostly used.

When the wires used in the Cottrell plant are covered with cotton or asbestos, the long fibres act as discharge points, which, owing to their fineness, are superior to metallic points. The Anaconda Copper Mining Company, Montana, U.S.A., use over 100 miles of chains suspended between plates. When the plates are thickly coated the current is cut off, and the dust falls into a hopper.

The Cottrell process has also been used to precipitate tar found in coal gas, preparatory to directly fixing the ammonia.

A further type of improvement which may be looked for is the better utilization of crude potash salts, which would be much better converted into sulphates than left as chlorides (p. 170). The ordinary salt cake furnace will suffice for such a purpose, and instead of wasting much of the sodium and magnesium salts mixed with the potash, these could be turned into the corresponding sulphates and exert their fertilizing value. Up to the present, little practical use has been made of sodium and magnesium sulphates, although Rothamsted has been showing for about 70 years that these materials are by no means to be despised as fertilizers.

The war has left Great Britain possessing much new plant and many novel industries. At the time when hostilities ceased, this country was manufacturing about 100,000 tons per annum of nitric acid and sulphur trioxide, with an efficiency

of about 93 % and 91 % respectively. There were also being manufactured about 60,000 tons of trinitrotoluene and 30,000 tons of cordite per annum. These factories have been erected on a semi-permanent basis, and could continue operations if some industrial use were found for their products. It is one of the problems of the future to convert some of this war enterprise into useful peace industry, and to this end the fertilizer trade might take some active part.

As regards the more intellectual side of the question, the view that Britain is superior to Germany in the possession of creative scientific power has always been maintained in modern times by students of philosophy and history. That this view has been a correct one was amply demonstrated by Pope in his Presidential Address of 1919 to the Chemical Society. Whilst Great Britain overcame its initial handicap by many novel scientific devices of military value, Germany did little more than use the elaborate plans which had been devised before the declaration of war. The brilliant position which Germany had held in applied science arose from the keen appreciation of the advantages of science exhibited both by the German people and by the German Government. Germany grasped the essential fact that rich economic rewards were to be gained from the systematic exploitation of scientific industry. Great Britain, however, continued to neglect scientific effort, and to devote its energies almost entirely to financial enterprise. It seems somewhat doubtful if the British people have learnt this important lesson of the war, and there is a great fear that they may return to their original neglect of scientific initiative.

The outlook for 1920 is a shortage of phosphates.

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Section III.—IMPROVEMENTS IN THE USE OF FERTILIZERS

The weary struggle during the long period of agricultural depression in the British Isles caused much land to pass into the hands of the pessimist, who endeavoured to farm in a method by which he could not lose, and by which the State stood to gain but little. The attempt to solve the problem by offering Parliamentary guarantees, gives rise to the serious danger that the drone who occupies good old corn land may easily make more out of it than the energetic man makes out of the acres of new land he breaks up, in his efforts to lay the foundation of future prolific food supply. The farmer needs for his operations not only land, but well-tilled and well-drained land, which can be treated with chemical fertilizers in a scientific manner. How much of this effort to improve soil fertility should be borne by the landowner needs to be carefully considered; the tenant farmer can hardly be expected to sink much capital on those fertilizers which will produce their best results after the lapse of many years. It is to the landowner's interest that the land should be put into good heart; that this can be done, even with the poorest land, has been shown time after time. At Cockle Park, in Northumberland, land which had a very low rental has, by comparatively simple means, been converted into at least an average pasture, and the value of the land has been markedly increased by the process. Much of the difficulty, in persuading the farmer to use a sufficient quantity of fertilizers, has been due to the lack of sufficient capital by the farmer, or, what is putting the same matter into other words, large numbers of farmers take farms which are too large for the amount of capital at their disposal. This difficulty is likely to become even more acute in the future,

because the rise in the amount of wages that must be paid by the farmer necessitates a larger bank balance, and therefore a larger capital. Added to the rise in the cost of labour, is the rise in the cost of materials, and a capital which was sufficient to enable a man to work a farm before the war is now quite insufficient for the task. It is very largely this difficulty of insufficient capital that prevents progress. It has been the habit of the fertilizer manufacturers in the past to do their share towards meeting this difficulty by providing very long credit for the payment of manure bills; but, with the rise in the interest payable on loans, the manure manufacturer may be compelled to raise his terms for this service. It seems probable that this custom will be extended in the future, unless some other means can be devised for providing the farmer with capital to carry on his holding, which has now become, in comparison with his capital, too large for him to manage. The increase in the cost of labour will compel the farmer more than ever to put into practice a lesson he has already fairly well learnt. Farmers have learnt to aim at a whole crop, knowing by experience that fractions of crops do not pay; the higher the cost of cultivation becomes, the more necessary it is for the farmer to obtain full crops from his land. The weather is out of his control, but by supplying sufficient amounts of fertilizers, he can diminish the effect of adverse conditions.

To enable full utilization to be made of the fertilizers, the farmer should have a more complete education in the science of his life-work. There are plenty of farmers with well-developed powers of observation who never pass another farm without learning something by looking at it; but, on the other hand, there are, unfortunately, many occupiers of land who look over their neighbour's hedge only to find fault, who take no trouble to learn from the practice of others, who never visit an experimental farm, and whose daily work exhibits much dull routine and little enterprise or thought. There is no more striking lesson than to travel in any part of the country and observe how one well-managed farm is bounded by many indifferently managed holdings. Sometimes

the farmer knows a great deal better than he performs, and the reason for his lack of performance is insufficient capital, indifferent health, or perhaps an unsuitable wife.

In considering the best use to which one can put fertilizers, one must remember that the great present need is food production, which is not the same thing as agriculture. In pre-war days that type of farming was considered best which produced a sufficient return on the capital invested with the least possible risk and trouble to the farmer and to the landlord. The British people looked to the world for its food, and to the Navy for its security. The land itself was merely a home farm, a convenient source of milk, vegetables and prime meat sufficient only for the needs of a small fraction of the population, but otherwise of little account as a contributor to the general stability of the country. Sir Thomas Middleton estimates that, in pre-war times, the food grown in the United Kingdom would have just kept the population from Friday evening to Monday morning in every week, and he alludes to the condition of farming in the country as being a " week-end " sort of farming. If we compare this with the policy that prevailed in Germany, we see that the German object was to keep under the protection of her guns the ground on which her corn grew and her cattle grazed, so that Germany grew nine-tenths of the food used, as against our one-fifth. The reason why Germany produced so much more food than Great Britain, was not that the yield per acre of her crops was greater, but that Britain was mostly under grass, whilst Germany had much land under the plough. We have, in this country, grass of varying quality, from a hill pasture, producing 2 or 3 lbs. of mutton per acre, to rich grazing pasture, on which a bullock may put on 3 or 4 cwt. live weight per acre in the season. Poor lowland pastures will yield about 20 lbs. of lean meat per annum, whilst medium pasture will give about 100 lbs. of meat per annum. The poor land at Cockle Park has, by judicious but economic management, been converted to this medium pasture condition, and produces now rather over that amount, but some of the really first-rate fattening pasture

in the country may produce 200 lbs. per acre per annum. A poor pasture may therefore be said to be such that 100 acres will provide the food for 2 or 3 persons, whereas in a rich pasture the 100 acres will provide food for 30 or 40 persons. On the other hand, 100 acres growing an average crop of wheat will provide food for about 230 persons for a year, assuming that the wheat was milled to about 80 % standard, and that the tailings and damaged grain were used for cattle feeding. Similar estimates for barley and oats allow food for about 160–180 persons per annum per 100 acres. Potatoes, on the average of the country, feed about 400 persons per 100 acres of land, whilst, adopting the allotment standard of 12 tons of potatoes per acre, about 800 persons could be fed on 100 acres of allotments. The amount of fertilizers needed to produce this result in the case of potatoes is much greater than the amount of fertilizers used for wheat, and wheat demands more fertilizers than pasture. Middleton, by averaging up the rotations practised in the United Kingdom before the war, estimates that the produce of the ploughed land of the country maintained about 84 persons per 100 acres. Although shipping tonnage is not so short as it was, it is still necessary to practise economy. The utilization of a larger quantity of fertilizers, with the production of more foodstuffs, will result in a reduction of the needed amount of shipping. Previous to the war, farmers depended far too much upon imported feeding stuffs for maintaining or fattening their stock. The farmer had the idea that the feeding stuffs, having served their purpose as foods, enriched the manure which he needed for his land, but such a method of obtaining manure was very expensive. Far better results can be obtained by the direct application of fertilizers to the land, resulting in increased supplies of home-grown food suitable for feeding the stock and improving the manure. The use of a large quantity of phosphatic fertilizers on pastures will keep them in good condition later on in the season, and will diminish the risk of a glut of meat at the end of the grass season, with a corresponding shortage in the spring. The future of fertilizers in Great Britain depends on the measures

adopted by that country for the production of home-grown food. If the British people revert to a foreign food supply regardless of security, then much of the land which has been ploughed up will fall back to indifferent grass; if they consider security, financial as well as military, they will be forced to grow a larger quantity of corn, and therefore employ a larger quantity of fertilizers. Such corn growing as Great Britain had before the war depended largely upon the conditions of this country which followed Waterloo. At that time corn prices were relatively high, yet farmers lost money and many became bankrupt. Nominally, landlords grew rich on the great rents they received; as a matter of fact, few grew rich, and the money saved was invested in permanent improvements on the land. The capital thus sunk resulted in a sufficient food supply being provided during many years for the rapidly growing industrial population of this country. The growth and prosperity of industrial England might never have occurred but for the care which landowners gave to the improvement of their estates, and to the extent to which they invested the proceeds of land in the improvement of the soil between 1760 and 1820. During the war rents have not been raised, public burdens have greatly increased, and interest on mortgages has risen. Occupying landowners have increased their capital, but the total volume of this increase is not great, and unless there is a transference of land to men who have made profits in other industries, it is difficult to see where the private capital necessary for the improvement of the land is to come from. During the war farm buildings, fences and other essential plant have fallen into disrepair, and large sums of money will be necessary to bring farms into a working state once more. During the war heavy debts have been incurred, the interest on which will be made easier to pay by any addition to the home-grown food. Yet, 90 years ago, after the first effects of the Napoleonic wars had disappeared, although farmers lacked artificial manures, were without pipe drainage, and had little machinery, Great Britain fed a larger population than she does to-day. The gross value of the produce of

100 acres of medium quality grass set aside for grazing cattle would amount to £400 per annum, but the same land, if put on to a four-course rotation, would produce £800 worth of food. If Great Britain can produce another £400 worth of food without causing other industries to suffer, the nation will have that amount more with which to pay its foreign debts. During the war there has been a great accession to the ranks of the workers of Britain, chiefly through the influx of women, many of whom will probably not leave. This increased supply of labour may mitigate some of the difficulties of the future. It is by the utilization of modern appliances, chemical fertilizers and machinery. that Great Britain must look in the future to enable the country to make full utilization of the land.

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PART VI.—CHEMICAL INSECTICIDES AND FUNGICIDES

SECTION I.—INORGANIC POISONS

IN addition to the need for supplying the plant with fertilizing ingredients, it is often found desirable to protect the crop from attack by insects, fungi or other living parasites. Beside the substances coming under that heading there are also some poisons employed either in the manufacture of dairy products, or during the process of cleaning on the farm, or on other special occasions connected with farming.

Mercury.—Excepting as mercuric chloride (corrosive sublimate), little use is made of mercury on the farm. In the ordinary preparation of mercuric chloride, mercury is first heated with sulphuric acid, the resulting cake mixed with salt, dried with precautions to avoid poisonous fumes and finally sublimed. Great care is taken to avoid admixture with traces of calomel and sulphuric acid, but for agricultural purposes the presence of these impurities is of no consequence. Solid mercuric chloride is not suitable for use on a farm, but solutions are required for disinfection when cases arise of abortion or other highly infectious disorders. The best strength of solution varies from 1 part of mercuric chloride in 500 of water to 1 part in 5000, to which may be added a little acid. For practical use, stronger solutions are kept ready to hand in glass bottles which should be provided with rubber stoppers attached by string to the bottle, to prevent loss, or more important still, to prevent the mercury-contaminated stopper being put into a wrong bottle. A good standard article is made from 5 parts of mercuric chloride, 5 parts of common hydrochloric acid and 100 parts of water. The same strength of solution

can be made by taking a saturated solution of mercuric chloride at 60° F. and adding 5 % of hydrochloric acid. Such a solution can be diluted with from ten to a hundred times its bulk of water, according to need. As a precaution against blunders it is advisable to colour the stock solution with a little indigo sulphonate or aniline blue. Mercuric chloride, in the presence of air and hydrochloric acid, slowly oxidizes many organic dyes, but indigo stands well.

Copper.—The copper compounds used in agriculture are made from copper sulphate. In the manufacture of copper sulphate, copper containing iron and sulphur is roasted with the addition of more sulphur if necessary, dropped into sulphuric acid diluted with water and the solution cooled till crystallization takes place. By adjusting temperatures it is possible to reduce the amount of iron entering into solution. In any case, some iron separates out with the copper in the form of $CuSO_4.3FeSO_4.28H_2O$. This compound decomposes at about 180° C. (350° F.), when ferrous sulphate free from copper crystallizes out. High pressure steam boilers permit this operation to be carried out. Even at atmospheric pressure, recrystallization of copper sulphate containing ferrous sulphate yields a crop of crystals containing much less iron. Considerable quantities of crude copper sulphate containing much ferrous sulphate is placed on the market. For some purposes these crude mixtures can be used in agriculture, but the general experience is against them, since the average cost of the copper contained exceeds that of the same amount of copper in good quality copper sulphate.

For most agricultural purposes, the physical condition of the sulphate of copper sulphate is very important. Large crystals are troublesome when making solutions on the farm. This difficulty can be removed by grinding, but the best method of dealing with the manufacture of copper sulphate for agricultural purposes is to crystallize quickly with agitation. For this purpose, a hot solution of copper sulphate containing ¼ % free sulphuric acid is run into a sheet copper vessel, surrounded with water. Agitation is best obtained

by blowing air through a copper pipe into the copper sulphate and through any pipe into the outer cooling water. The air incidentally helps to oxidize the ferrous sulphate in the crude copper sulphate and prevents its crystallization; whilst in the outer vessel the air stream evaporates some of the water with a lowering of temperature and economy of cooling water. The water in the outer cooler must in the end be replaced by cold water to reduce the temperature. By these means a very fine grained crystal almost free from iron can be obtained. These fine crystals dissolve readily even in cold water.

Solutions varying from 2–5 % are used for "pickling" corn to prevent attacks of "rust" in wheat and other similar fungoid parasites. Solutions of the same strength are used to destroy "charlock," "runch," or wild mustard. About 40–70 galls. of 3 or 4 % copper sulphate solution are sprayed over an acre of infested wheat, barley or oats when the charlock begins to come into flower. Little harm is done to the corn, but the charlock is burnt up and quickly dies.

Copper Compounds.—Except the cereals, most plants are injured by copper sulphate unless some other substance is added. As a rule the additional material is basic and is added in sufficient quantities to precipitate the copper from solution. Burgundy mixture is made from copper sulphate and sodium carbonate and is applied as a spray to potato plants about July, followed by a second application a few weeks later. For spraying one-third of an acre, 4 lbs. of sulphate of copper are stirred up with about ten galls. of water in a wooden barrel, capable of holding 40 galls., and then diluted to 35 galls. In a separate vessel, 5 lbs. of washing soda are dissolved in 5 galls. of water and the mixture slowly poured, with agitation, into the solution in the barrel. Burgundy mixture is of a bright blue colour and only settles slowly; when a day old it becomes green and settles. The mixture should be sprayed in the blue colloidal form, when it adheres well to the leaves of the potato plant.

Bordeaux mixture is made by slaking 2 pounds of freshly

burnt quicklime with a little water, diluting to 5 galls. and pouring into 35 galls. of copper sulphate solution, made as above. As quicklime varies in composition, this recipe is not always satisfactory and some manufacturers prepare a paste ready made for the use of farmers. Many difficulties are encountered in the manufacture and use of such mixtures and it appears to be more generally useful to employ the Burgundy mixture which is easy to make on the farm. The labour on the farm can be reduced if the correct quantities of copper sulphate and washing soda are weighed out into small sacks and sold ready for use. As fruit trees are apt to be scorched by Burgundy mixture, a special Bordeaux mixture is preferred; for this purpose the amount of copper sulphate in the above recipe is reduced to 3 lbs. and the lime increased to 3 lbs. Some users prefer to pour the copper sulphate solution into the milk of lime. When copper sulphate is mixed with basic substances, copper hydrate and basic copper sulphate are formed, the relative proportions depending on the amount of basic substance added. In the case of Burgundy mixture, the presence of carbonic acid causes a basic carbonate to be formed, which slowly reacts with the carbonate left in solution, ultimately forming green crystalline malachite. Treacle and other adhesives are sometimes used in conjunction with any of the above copper sprays. The introduction of soap into such mixtures causes a great change in their chemical and physical properties since copper soaps are formed.

Ammonia and Copper.—For horticultural purposes mixtures containing copper sulphate and ammonia are often favoured. For spraying chrysanthemums and other flowers a green adherent compound is not suitable. As mixtures containing copper and ammonia are not readily made on the spot, it is better to purchase a ready-made mixture. A good recipe is 10 lbs. of copper sulphate, 15 galls. of water and 1½ galls. of ammonia (·880 gravity). Such a stock solution must be diluted so that one pint makes 2–4 galls. for spraying the flowering plants: a dilution of from 1 : 16–1 : 32.

The deep blue liquor obtained by adding ammonia to copper sulphate contains the compound $CuSO_4.4NH_3.H_2O$ called cuprammonium sulphate. When dried on the leaves of the plants to which it has been applied by spraying, some of the ammonia is evaporated and ammonium sulphate and basic copper sulphate is left behind. The ammonium sulphate washes off with ease and the basic copper sulphate does not possess the same power of adhesion that is to be found in the lime and soda varieties of basic copper sprays.

Arsenic.—White arsenic, arsenious acid, As_2O_3, is used in sheep dips. From 2–10 lbs. of sulphur, 1 lb. of arsenic and ½ lb. of washing soda are ground up. The washing soda may be replaced by "dry soap," a mixture of soap and soda. The mixture rather improves on keeping, as the arsenic slowly combines with the soda to form arsenite of soda. The quantity stated makes 50 galls. of dip. Whilst any sunk bath might be made to serve, special dipping baths are on the market which are very economical to use both as regards material and labour. Sodium arsenite slowly oxidizes to sodium arsenate. Sunlight, aeration and the presence of water increases the speed of the reaction. Very old dips containing soda and arsenic may, therefore, be partly oxidized to arsenate. As the arsenates are less poisonous than the arsenites, old dips may have less value than new ones. It is for this reason that a mixture of sodium carbonate and arsenious acid is better than ready-made sodium arsenite, as it takes much longer to deteriorate.

Lead Arsenate.—A very effective and safe remedy for caterpillar attacks is a spray of ¼ or ½ % lead arsenate. To prevent scorching the leaves of fruit trees, it is essential that no marked excess of either lead or arsenic acid should be present. As all the materials used are of varying composition and very poisonous, it is better to have the lead arsenate in the form of a paste that can readily be diluted.

Arsenious acid can be oxidized by nitric acid or, in the presence of water, with chlorine. Sodium arsenate can be then prepared and crystallized. The resulting crystals consist of $Na_2HAsO_4.7H_2O$; but if crystallized at low temperatures

the dodecahydrate is also obtained. A little over 1½ times its weight of lead acetate is added to produce a paste of lead arsenate. Without a knowledge of the exact composition of the ingredients, a safe paste is hard to produce. A pure heptahydrate of sodium arsenate contains 59·6 % of anhydrous sodium arsenate, whilst the pure dodecahydrate contains 46·27 %. It takes 3·056 parts of pure crystallized lead acetate to precipitate 1 part of dry sodium arsenate.

Lead arsenate can also be made more directly. Four parts of arsenious acid are added to 3 parts of nitric acid of 1·35 specific gravity. On the large scale heat is evolved and much nitric acid is given off, much of which can be condensed in a tower full of wet coke. On the small scale external heat and more acid may be needed. In either case a hot syrupy liquid is left consisting of arsenic acid containing traces of arsenious acid and some nitric acid. The nitric acid must be reduced by heat till it does not exceed 1 % of the mass. Fourteen parts of litharge are now added with 10 parts of water, when slight heat is evolved. Warming the mass hastens the combination till only lead arsenate is left with a little lead nitrate. If the amount of nitric acid was too great a little sodium carbonate must be added, till neutral to litmus. If the amount of nitric acid left in the arsenic acid was too small the reaction becomes very slow. The resulting paste will show at once if the right quantity of water was added. The compound actually used is $Pb_3(AsO_4)_2$ mixed with water.

Ferrous Sulphate.—This material in the crystallized form, $FeSO_4 . 7H_2O$, is produced as a by-product in the separation of copper in the wet way, by throwing iron scrap into weak solutions of copper sulphate. The ferrous sulphate can be recovered by crystallization. Tin plate works also contribute to the supply.

Ferrous sulphate can be used in sprays in the same way and for the same purposes as copper sulphate. It is, however, much less active, and almost saturated solutions must be used. The addition of free sulphuric acid increases the germicidal effect. The spray from ferrous sulphate is ruinous to clothing.

Zinc Chloride.—The process commonly called "Burnettizing" from the name of the inventor, consists in preserving timber by a 2 % solution of zinc chloride, forced in under pressure. A strong solution of 50 % of zinc chloride is made by dissolving scrap zinc in hydrochloric acid and evaporating to a density of 1·56. The excess of hydrochloric acid is given off and may be condensed. This strong solution can be diluted as required.

Potassium and Sodium Permanganate.—These disinfectants work by oxidation. They are made by heating the carbonate of the appropriate alkali metal with manganese dioxide and some oxidizing substance such as potassium chlorate or potassium nitrate. The mass is boiled with water and enough acid added to turn the solution pink. The solution is then crystallized. Potassium permanganate is easier to crystallize than the corresponding sodium salt The permanganates can also be made electrolytically.

Barium Carbonate.—This insoluble substance occurs as a mineral and only requires grinding. Ten parts of barium carbonate, 10 parts of sugar, 10 parts of oatmeal and 1 part of aniseed, make a good poison for rats. The poison should be placed where dogs, hens and pheasants are not likely to find it. Barium carbonate is insoluble in saliva, but dissolves readily in gastric juice.

Alkali Salts.—Potassium and sodium nitrates are used in pork pickle. Sodium chloride is a well-known weed killer. The purity of the salt for weed killing is of no consequence.

Sodium bicarbonate is used sometimes in butter manufacture. When only a few cows are kept at a farm, cream is allowed to accumulate for a few days before churning. In summer weather the cream so stored may be over-ripe, butter be difficult to make satisfactorily and the product be rancid to taste and smell. The bitter flavour and rancid smell are due to butyric and other similar acids. Butyric acid is more soluble in fat than in water, hence washing with water only removes it slowly. If, however, sodium bicarbonate be added, sodium butyrate is formed which is

more soluble in water than in fats. Hence, washing easily removes the rancidity. Ordinary sodium bicarbonate is quite suitable.

Sodium hydroxide is used in solution to rid trees of aphis and many other pests. A ½ % solution may be sprayed on to trees, which have strong thick bark, to kill insects and fungi. It is, however, mostly used in conjunction with soap (see p. 251).

Boron Compounds. — Excepting in preservatives of cream, boron plays little part in agriculture. For the preservation of cream a mixture of equal parts of crystallized boric acid and borax is better than either alone. Cream so preserved must be labelled accordingly. From ¼ to ½ % boric acid in the cream is sufficient.

Sodium Silicate.—Water-glass is made by fusing fine, white sand and sodium carbonate in the proportions of 170 parts of sand to 100 parts of soda ash. Such a mixture gives a ratio of $3SiO_2 : Na_2O$. Sometimes the ratio is reduced to $2SiO_2 : Na_2O$, or about 110 parts of sand to 100 of soda ash. The fused silicate needs long boiling under pressure to obtain a solution. Alternatively finely ground flint or other siliceous material is boiled under pressure with caustic soda. The latter process does not easily yield the higher ratios of silica. The resulting solution is sold as a thick syrup containing 37 % silica and 16 % of soda (Na_2O) and approximates to a hydrated form of NaH_3SiO_4.

The thick syrup diluted to about one-fifteenth strength is used for preserving eggs. It may also partly replace soda or soap in sprays, *q.v.* pp. 245, 251.

Sulphides and Polysulphides.—These materials are very useful insecticides. By the action of the carbonic acid generated by any injurious insect or destructive bacterium, hydrogen sulphide is liberated and free sulphur is precipitated in a fine condition. The former is directly poisonous and the latter chokes the breathing pores of insects. As these sulphides often contain free alkali, the protective wax coatings of many insects fails in its waterproofing properties and the insect may be drowned.

Lime Sulphur Wash.—This is one of the simplest and

cheapest of the sulphide class. It is made by boiling 50 lbs. of lime, 100 lbs. of sulphur and 100 galls. of water for about three hours. The resulting liquid is allowed to settle, which it does very quickly, and the clear orange-coloured liquid is syphoned off into well-corked bottles. The liquid has a gravity of 1·16 and contains 9·7–9·8 % sulphur precipitable by mineral acids and 2·8 % lime alkaline to methyl orange. Some brands on the market are double the above strength. The stock solution is diluted ten or twenty times for spraying.

The quantities of material used and found in the product show that the reaction during manufacture is :—

$$3CaO + 12S = 2CaS_5 + CaS_2O_3$$

On adding hydrochloric acid all the sulphur is precipitated and after boiling may be filtered off on a Gooch crucible and weighed. On titrating with methyl orange only the CaS_5 reacts. On passing carbon dioxide into the spray liquid the CaS_2O_3 is not decomposed but the CaS_5 gives $CaCO_3 + H_2S + S_4$.

Liver of Sulphur, Potassium Sulphide.—This well-known insecticide is made by heating potassium carbonate and sulphur and pouring the fused mass on to a cold surface. The material easily dissolves in water to make a solution of about ¼ %. To this is usually added an equal amount of caustic soda, sodium carbonate or soap. Strong solutions can be prepared, but must be well corked and bottled until they are needed for dilution.

The potassium in the above can be replaced by sodium without any decrease in power. The advantage of using sodium or potassium in preference to calcium only occurs when it is desirable to add some alkali or soap to the poly-sulphide. The admixture of alkali or soap is particularly useful for destroying the waterproofing of the wax coated cuticle of the insect (see pp. 246, 251). Lime sulphur wash has little power in this respect and hence insects shed the fluid off their backs like the proverbial duck. Strong solutions of liver of sulphur can also be made by boiling 70 lbs. of

caustic soda with 100 lbs. of sulphur and 100 galls. of water.

Chlorine.—In the form of chloride of lime or bleaching powder, chlorine finds its way into use on the farm. For washing cow-byres, latrines, etc., it is very useful. Bleach is fully described in the volume on "The Alkali Industry" by Partington.

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Section II.—ORGANIC POISONS

Carbon Disulphide.—This poisonous substance is manufactured by passing sulphur vapour over red-hot charcoal. Carbon disulphide is a heavy liquid giving a heavy vapour and can be used to destroy weevils in corn. A small depression is made at the apex of a heap of corn and the carbon disulphide poured in; the heavy vapour sinks to the bottom of the heap. The liquid may also be used to pour down the burrows of foxes, rabbits, etc.; it has been employed to destroy wire-worms and other grubs in the soil. In its action carbon disulphide is at first anæsthetic; insects often recover momentarily from its influence, and crawl about, but collapse finally in a few minutes. It is much more powerful as a poison for insects than naphthalene, but not so strong as carbon tetra-chloride.

Thiocarbonates and Perthiocarbonates.—When carbon disulphide is agitated with sodium sulphide, a thiocarbonate is formed, Na_2CS_3, but if free sulphur is also present the reaction occurs more rapidly and the compound, Na_2CS_4, sodium perthiocarbonate is formed. In presence of carbonic acid these substances give off carbon disulphide, hydrogen sulphide, and in the latter case sulphur as well. A crude mixture containing thiocarbonate, perthiocarbonate and sulphide has been used for spraying vines and potatoes.

Formalin.—This powerful antiseptic is a 40 % solution of formaldehyde in water. It is made by passing air under pressure through a "carburetter" supplied with methyl alcohol. The methyl alcohol need not be more concentrated than 90 %, but the temperature must be raised to about 45–50° C. (110–120° F.) to obtain a high enough proportion of alcohol vapour. The air and alcohol vapour pass through a catalyzer consisting of copper gauze at a low red heat. Heat is necessary to start the reaction, but the heat evolved

in the process is enough to maintain the temperature. The vapours pass to a condenser and scrubber down which a little water flows. The liquid passing away from this condenser is formalin. The gases pass to a condenser, where the excess of methyl alcohol is recovered, and then on to a scrubber where water washes the remaining methyl alcohol out of the waste gases. The recovered alcohol goes into circulation once more. The efficiency is only about 50–60 %.

Formalin is diluted with from 100–10,000 times its volume of water before use. Strengths varying between 1 in 1000 and 1 in 10,000 have been used to destroy fungoid spores on grain without reducing the germinating power of the seed.

Cyanides.—Prussic acid is used for fumigating fruit trees and greenhouse plants. Many insect pests can be eradicated by this means, but much caution is needed to prevent accident. The prussic acid is manufactured on the spot as vapour by acting on potassium or sodium cyanide with either sulphuric or phosphoric acid. Fairly pure sodium cyanide is sometimes sold as 120 % potassium cyanide, that being the equivalent values of the two salts. When practicable the cyanide should be placed in a fairly open vessel, the doors of the greenhouse closed, and the acid admitted by a tube from outside. Failing the necessary facilities for such treatment, a weaker acid such as phosphoric acid is employed, when the operator has more time to get away. A better safeguard is to enclose the cyanide in zinc capsules, which dissolve slowly in the sulphuric acid and allow time for closing the doors. In the U.S.A. a tent is placed over a fruit tree and a basin of cyanide set on the ground. It is not then difficult to add the acid and close the tent quickly. In mushroom cellars the addition of the acid from outside can usually be arranged for. A general adoption of a " carton " system would make this method of fumigation more practical. Correct quantities of cyanide in thin zinc cases, accompanied by the correct amount of acid in glass bottles, would enable the horticulturist to exterminate insects with confidence.

Petroleum.—When petroleum is distilled, a moderately high boiling fraction is used for lighting purposes under the name of paraffin oil or kerosene. Paraffin oil only forms temporary emulsions with water when violently agitated, but by the addition of colloids, or fine precipitates, a semi-permanent emulsion can be obtained. The most convenient emulsifying agent is soap. A good stock solution can be made by dissolving 1 lb. of caustic soda and 10 lbs. of soap in 10 galls. (100 lbs.) of water, adding 10 galls. of paraffin and emulsifying by forcing all the liquid through a finely perforated plate; a syringe will serve. The stock solution keeps well and can be diluted with 10 times its bulk of water when required. The spray can be used on vegetables and fruits, which would be poisonous if mercury, copper, lead or arsenic were used. In a few days the smell of the paraffin disappears. Even the burrowing grub that attacks parsnips can be killed off by this treatment.

Soap.—For destroying aphis even 1 % of soap is successful, and for caterpillars 2–3 % will serve. The insecticidal power of the solution can be increased by adding ¼–½ % caustic soda.

A useful dry soap powder is made by grinding together a hard soap and soda ash. The proportions used vary, but 2 or 3 parts of soda ash to 1 part of soap is a useful mixture. Of such a dry soap, 1–2 lbs. per 10 galls. makes a useful spray for aphis and many small grubs. This dry soap may also be used in place of the mixture of soap and caustic soda employed with paraffin in the above paraffin emulsion.

Rosin soaps are very suitable for grinding up with soda ash for making dry powders for spraying. Such preparations are more active than those made from pure fat soaps. The rosin used chokes the breathing pores of small grubs whose cuticle is wetted and injured by the accompanying alkali. Tar acids and other disinfectants can also be introduced into the dry soap mixtures to produce more powerful results.

Tar Acids.—Phenol, cresol and their homologues are all

useful germicides, but the higher phenols are much more poisonous than the simpler phenols. When coal is distilled, a tar is produced, which on redistillation yields a fraction called creosote, which, on extraction with caustic soda, yields a mixture of tar acids in combination with the soda employed. On treatment with acids the tar acids are set free. Pure phenol is oxidized by bacteria in the soil to trihydroxy-glutaric acid; the higher phenols are very resistant to bacterial action. Winter sheep dips are generally made from 2 parts of creosote and 1 part of a 20 % solution of caustic soda. The creosote must be rich in tar acids, for which purpose a Midland or South Country gas tar creosote is the most suitable. Blast-furnace creosotes contain much hydrocarbon, which checks emulsification, whilst North Country gas tar is rich in naphthalene, which has a similarly retarding influence. The addition of wood tar or soap increases the emulsification of the mixture. Crude tar containing much free carbon is quite unsuited for the manufacture of sheep dips, as the carbon is not easily removed from the wool.

Creosote.—The middle fractions obtained on the distillation of coal tar are used for preserving timber. The preservative effect of creosote depends partly upon the proportion of tar acids, but also upon the more complex hydrocarbons. The result is complicated by the double action of waterproofing and poisoning that takes place at the same time, both of which duties are performed by most of the ingredients present. Preservation of timber may be carried out by merely painting on the surface, when the benefit is uncertain. By immersing timber in hot creosote much better penetration is obtained, but the amount of creosote used is large. By the pressure process creosote is forced into the vessels of the wood and, after soaking, the excess of creosote may be removed by reversing the pumps. An alternative method is to employ emulsification. By mixing creosote, water and caustic soda, so as to produce not less than a 20 % creosote and ¼ % soda emulsion, deep penetration of the fibres of the wood can be obtained by

hot treatment in an open tank. Such mixtures can also be painted on with a brush. For the emulsification processes, a creosote should be used which is rich in tar acids and poor in hydrocarbons.

Sulphonated creosotes are also used. For this purpose creosote is heated with 2 or 3 % of its bulk of strong sulphuric acid. After sulphonation a creosote will mix with water to an emulsion. Sulphonated creosotes can also be applied with a brush for fence work.

Naphthalene.—During the process of distilling coal tar, there is a period, a little over 200° C. (400° F.), when the distillate solidifies in the condenser. Also, on cooling many distillates, naphthalene crystallizes out. The crude naphthalene so obtained is sometimes known as "creosote salts," and is of the consistency of brown sugar. All forms of naphthalene are slightly greasy and apt to stick together in lumps. To avoid stickiness during application on the land, naphthalene is often mixed with some dry material, such as boiler ashes, waste lime, sawdust, etc. For this purpose the naphthalene should be melted and poured on to its own weight of ashes or other drying material and then ground in a mill. Insects dislike naphthalene intensely and try to get away from it as fast as they can. If unable to avoid it they usually ultimately succumb to its effects.

Gas Lime.—This well-known means of destroying many pests in the soil is now only produced in small amounts owing to improved methods of gas purification. It has been described on p. 54.

Tobacco.—Waste tobacco is used for insecticides. The strength varies to a great extent. 2 lbs. of waste tobacco added to 10 galls. of water makes a good spray. Strong extracts can also be prepared by boiling up tobacco and water at the rate of 2 lbs. to the gallon. After straining off the liquor, the tobacco should be extracted with a further supply of water; the weaker extract obtained is then used to extract fresh tobacco. In this way more economical use can be made of waste tobacco.

Quassia.—The chips of wood of Picraena excelsa are

boiled for 8 hours in 5 times their weight of water, the liquor poured off, and the chips again boiled with the same amount of fresh water. The second weak extract is used for fresh chips. The extract is treated with enough soap to equal one-half the weight of quassia chips taken. The strong extract thus obtained can be diluted with 10 or 20 times its weight of water as required. The chief use of quassia is to remove aphis.

Pepper.—Waste pepper can be extracted with water in the same way as quassia. Pepper can also be used dry by dusting it on to gooseberries and other fruits infested with caterpillars. Red pepper is more potent than black pepper for such purposes.

Pyrethrum, Persian Insect Powder. — Seeds of Pyrethrum roseum or Pyrethrum carneum (Chrysanthemum coccineum or Chrysanthemum cinerariaefolium) are sown in May and the flowers collected when ready, which may not occur till the following summer. The insecticide consists of the pollen from the male flowers. Care should be taken not to heat the powder either by sun heat or fire, as the poison is volatile. The poisonous principle is soluble in alcohol; an extract can be made in a percolator by slowly allowing methylated spirit to trickle down a long column of pyrethrum powder loosely packed in a tube. The effluent spirit should weigh about the same as the powder taken. The alcoholic extract may be diluted with water up to 300 times its bulk and sprayed on plants infested with caterpillars. Pyrethrum powder must not be extracted hot, as the poisonous ingredients are partly decomposed.

Hellebore.—The rhizome of Veratrum album is dried and ground to powder to produce hellebore powder. The powder is mixed with 300 times its weight of water and used as a spray for biting insects. After a few days' exposure to air the poisonous properties disappear and render the fruits or other edible parts of plants safe to use.

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